

# ABSTRACT

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The recovery of actinides using solvent extraction technique involves use of diluent, leading to generation of secondary liquid waste. Literature data on the extraction and recovery of actinides using supercritical fluids are relatively scarce; data for the following is limited or not available: (i) recovery of actinides from a dissolver solution of spent nuclear fuel (ii) pre-concentration and recovery of actinides from aqueous waste stream (iii) selective extraction of uranium over thorium (iv) recovery of actinides such as plutonium and uranium from chloride salt waste of pyrochemical processing. The main objective of the present study is to develop supercritical fluid extraction (SFE) based methods (an alternate to solvent extraction technique) for the recovery of actinides from different matrices with minimum generation of liquid secondary waste.

The development of an SFE method for the recovery of actinide ions involves: (a) identification of actinide specific ligands (b) selection of ligand based on the nature of matrix, i.e. recovery of actinides from diverse matrices such as solid matrices (cellulose, pyrochemical inorganic salts) and liquid matrix (nitric acid medium) – this is quite crucial as recovery of actinides from various matrices depends on their interaction with the base material of the matrix (c) solubility of actinide specific ligands of interest in supercritical carbon dioxide (SCCO<sub>2</sub>) medium and optimization of experimental conditions, namely, temperature, pressure, co-solvent composition and (d) use of SCCO<sub>2</sub> containing ligand for recovery of actinides.

In connection with the above, solubility of variety of ligands from the family of trialkyl phosphates, dialkylalkyl phosphonates, *N,N*-dialkylamides and quarternary ammonium based ionic liquids was measured as a function of pressure, temperature and in some cases as a function of co-solvent composition. These compounds were chosen

based on their ability to extract actinides as (i) neutral solvates (trialkyl phosphates), (ii) extraction from lean streams (stronger and more basic extractant, phosphonate based molecules), (iii) neutral solvates with better properties to radiation (amides) and (iv) extraction through ion-pair complexes (quarternary ammonium compound). The solubility data of ligands are correlated using various semi-empirical equations; new models were developed for the correlation of solubility of liquid solutes in  $\text{SCCO}_2$  medium in the presence of co-solvents.

Based on these studies, SFE based methods were developed and demonstrated for the recovery of actinides from diverse matrices of the following (i) extraction of uranium, thorium from solid matrices as well as from acidic waste medium; (ii) selective extraction of uranium from thorium using  $\text{SCCO}_2$  containing branched trialkyl phosphates (iii) selective extraction of uranium from representative fission products using  $\text{SCCO}_2$  containing phosphonates and (iv) recovery of plutonium and uranium from chloride salt matrix using  $\text{SCCO}_2$  containing trioctylmethylammonium chloride. Preliminary studies were also carried out towards scaling-up of a typical SFE method for the recovery of uranium from chloride salt matrix.

These studies have established promising applications of supercritical fluid based extraction based methods for the recovery of actinides from diverse matrices.

# SYNOPSIS

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The nuclear fuel cycle is associated with the series of process steps beginning from uranium mining, uranium enrichment, fuel fabrication, reactor operation, spent fuel reprocessing and waste management. Conventional methods such as liquid-liquid extraction, ion exchange and precipitation based techniques are extensively employed for separation and purification of actinides. However, use of these well-established methods lead to generation of secondary liquid waste. Therefore, there is strong impetus for the development of eco-friendly solvents that can reduce the waste generation and with reduced radiotoxic burden to the environment. The most prevalent of these solvent systems include supercritical fluids [1]. Supercritical fluid extraction (SFE) is a technique that uses a supercritical fluid (SCF) as a solvent for the extraction/recovery/separation of an analyte of interest from a matrix with minimum generation of liquid secondary waste, as CO<sub>2</sub> becomes gas after the extraction. SFE has many advantages over conventional liquid-liquid extraction and is a potential alternate technique to conventional liquid-liquid extraction [2].

SFE using carbon dioxide is widely employed for the extraction of a variety of compounds from both solid and liquid matrices. Several industrial plants are in operation for decaffeination of coffee, extraction of hop constituents, oils from leaves, fruits, seeds, spices etc. [3]. SFE of heavy metals, lanthanides and actinides from different matrices has been studied using SCCO<sub>2</sub> containing various ligands [4-6]. SFE based methods are also developed and demonstrated from our laboratory for the recovery of actinides [7]. The supercritical extraction of metal ions demands extensive knowledge on the solubility of ligands in SCCO<sub>2</sub> medium. The direct extraction of metal ions using neat SCCO<sub>2</sub> is not feasible because of weak solute-solvent interaction and charge neutralization

requirements [8]. However, when metal ions are complexed with suitable ligands, the resulting metal-ligand complexes become quite soluble in  $\text{SCCO}_2$  medium [9]. Thus, the solubility of ligand as well as that of metal complex in supercritical carbon dioxide medium plays an important role in designing a SFE process of metal ions.

Thus the use of SFE method for recovery of actinides can result in minimum generation of liquid secondary waste compared to traditional separation techniques. The literature data on the extraction and recovery of actinides ions using supercritical fluids are very limited. There is not enough SFE data in the literature for (a) recovery of actinides from dissolver solution of spent fuel and (b) for pre-concentration and recovery of actinides from aqueous waste stream. Use of pyrochemical-high temperature electrochemical process for recovery of actinides also results in the generation of salt waste containing precious actinides and there is no literature available for their recovery. Thus the motivation behind the work is to explore use of SFE based methods for the recovery of actinides from such waste streams and matrices.

The measurement of solubility of ligand in supercritical carbon dioxide is the first and fundamental step towards achieving the above objectives. Hence solubility of variety of ligands namely, trialkyl phosphates, dialkylalkyl phosphonates *N,N*-dialkylamides and quaternary ammonium based compounds are measured in  $\text{SCCO}_2$  medium. The solubility data are correlated with various semi-empirical equations. Subsequently,  $\text{SCCO}_2$  containing ligands are examined for the recovery of actinides from various waste matrices such as (i) recovery of uranium from nitric acid medium (ii) selective recovery of uranium from fission product elements and (iii) extraction and recovery of actinides from pyrochemical chloride salt matrix. The actinide specific ligands are chosen based on the solvent extraction literature data. Among the actinide specific ligands, further they are chosen based on the nature of matrix in which actinides are sorbed / complexed. For e.g. actinides in aqueous medium can be recovered using neutral extractants / ligands (trialkyl

phosphates / dialkylalkyl phosphonates); actinides in lean streams can be pre-concentrated using stronger actinide specific dialkylalkyl phosphonate based ligands; recovery of actinides from chloride salt matrix demands use of ligands which are capable of forming ion-pair complex with actinides, e.g. quaternary ammonium ligands e.g. TOMAC. Thus appropriate ligands are chosen and employed for the recovery of actinides from diverse matrices.

Several semi-empirical models are available in the literature to correlate the solubilities of solid and liquid solutes in  $\text{SCCO}_2$ . However, models to correlate the solubility of liquid solutes in  $\text{SCCO}_2$  in the presence of co-solvent are scarce. Two new models have been developed to correlate the solubilities of liquid solute in  $\text{SCCO}_2$  in presence of co-solvents, using association theory based on Wilson and van Laar activity coefficient models. These new models have been successfully employed for the correlation of solubility of trioctylmethylammonium chloride (TOMAC) in  $\text{SCCO}_2$  in presence of co-solvents.

This thesis is divided into eight chapters and a brief description of each chapter is given below

## **Chapter 1: Introduction**

This chapter deals with the basic introduction about separation sciences, its significance in the nuclear industry and need for the development of green separation techniques. A brief introduction to supercritical fluids and their advantages over conventional extraction using organic solvents are presented. The emergence of supercritical fluid extraction based technique as an alternative to conventional separation techniques in nuclear fuel cycle is highlighted. The importance of theoretical and experimental aspects of supercritical fluids to develop a SFE process is discussed. The necessity for solubility measurements on actinide specific ligands and need for use of

semi-empirical equations for solubility correlations are discussed. Current literature status on solubility measurements and SFE of actinides from various matrices are discussed.

The major motivation of the present study, i.e. developing supercritical fluid extraction based methods for recovery of actinides from diverse matrices is highlighted. The objectives, gap areas, and methodology followed towards achieving these are discussed.

## **Chapter 2: Experimental methods and semi-empirical models**

Chapter 2 is composed of two sub chapters. Chapter 2(a) provides a brief overview of chemicals, instruments, experimental set-up and general experimental procedures adopted in the present study. The synthesis and characterization of various ligands employed in the present study are discussed. The general procedure adopted for the solubility measurements is discussed. Validation of experimental procedure employed for the solubility measurement is described. The methodologies for the estimation of actinides using high pressure liquid chromatograph (HPLC) and liquid scintillation counting (LSC) technique are presented. Various semi-empirical models employed for the solubility correlations are described. Chapter 2(b) deals with various semi-empirical models employed in this thesis for correlating experimental solubilities.

## **Chapter 3: Experimental determination and correlation of solubility of trialkyl phosphates in supercritical carbon dioxide**

Chapter 3 deals with the experimental determination and mathematic modeling of solubilities of trialkyl phosphonates in  $\text{SCCO}_2$ . Trialkyl phosphates are candidate materials (ligands) in nuclear fuel reprocessing and hence the solubilities of a series of trialkyl phosphates in  $\text{SCCO}_2$  medium were measured at 313- 333 K with pressure ranging from 10-25 MPa and the results are discussed. The experimental solubilities are correlated using different semi-empirical equations such as Chrastil equation, Mendez-Teja (MT) model and association theory based van Laar activity coefficient model and

the results are presented. This approach provides an easy method to estimate unknown solubilities of other members of trialkyl phosphate series as well as to predict the solubilities of these compounds at different temperatures and pressures.

#### **Chapter 4: Solubilities of dialkylalkyl phosphonates in supercritical carbon dioxide**

Dialkylalkyl phosphonates have found renewed interest in the selective extraction of actinides from dilute waste streams. This chapter describes the solubilities of two dialkylalkyl phosphonates, namely, dibutylbutyl phosphonate (DBBP) and diamylamyl phosphonate (DAAP) in  $\text{SCCO}_2$  medium and correlate solubilities using various fundamental properties of supercritical fluids. Solubilities of dialkylalkyl phosphonates are correlated using MT model, Chrastil equation, solution theory with Wilson activity coefficient model and association model based on van Laar activity coefficient model and results are explained in detail. Comparison among these models revealed that the association model with van Laar activity coefficient model provides better solubility predictions.

#### **Chapter 5: Solubility of trioctylmethylammonium chloride in supercritical carbon dioxide with co-solvent and development of new models for ternary solubilities**

Chapter 5 is divided into two sub chapters. Chapter 5(a) deals with the measurement of solubility of trioctylmethylammonium chloride (TOMAC) in  $\text{SCCO}_2$  in the presence of different co-solvents. Recovery of actinides from complex salt mixture demands use of ion-pair reagents / ionic liquids and in this context, solubility studies on TOMAC in  $\text{SCCO}_2$  are carried out at different temperatures and pressures. The influence of co-solvent and its concentration on the solubility behavior have been studied. The solubility of TOMAC in neat  $\text{SCCO}_2$  medium is successfully correlated using semi-empirical models. Chapter 5(b) describes the development of new models for the correlation of solubility of liquid solutes in  $\text{SCCO}_2$  in the presence of co-solvents (ternary solubilities) and two new models are derived.

## **Chapter 6: Solubility of *N,N*-dialkylamides in supercritical carbon dioxide: Experimental and modeling approach**

The dialkylamides are potential alternate candidates to trialkyl phosphates for actinide recovery and extraction, as these ligands are resistant to hydrolysis and radiolysis, innocuous nature of their degradation products and possibility of complete incineration leading to reduction in the liquid secondary waste. Hence the solubility behavior of three straight chain amides (dihexylhexanamide, dihexyloctanamide and dihexylhexanamide) and three branched amides (di-2-ethylhexylacetamide, di-2-ethylhexyl-*iso*-butyramide and di-2-ethylhexylpivalamide) are examined in SCCO<sub>2</sub> medium. The experimental solubilities are correlated using various semi-empirical models.

## **Chapter 7: Supercritical fluid extraction studies of actinides from different matrices using modified supercritical carbon dioxide**

The applications of SFE technique towards actinide recovery from various matrices are discussed. Actinides such as uranium, thorium and plutonium are to be recovered from aqueous medium to minimize the radiotoxicity on the liquid waste; similarly, separation of uranium from thorium is of primary importance in thorium fuel cycle; chloride salt waste arising from pyrochemical process contains residual actinides and these have to be removed in order to minimize the volume of high level liquid waste. An attempt has been made in this study to employ SCCO<sub>2</sub> containing ligands for recovery of actinides from these matrices.

This chapter consists of three sub chapters. Chapter 7(a) focuses on the extraction / recovery of actinides from nitric acid media Chapter 7(b) mainly emphasizes the use of TiAP and DAAP for the selective extraction of uranium from fission products. Chapter 7(c) deals with the recovery of actinides from pyrochemical salt matrix using SCCO<sub>2</sub> containing TOMAC. This chapter also describes the semi-preparative scale extraction of



uranium from salt matrix. This study is first of its kind towards the recovery of actinides from chloride salt matrix.

## Chapter 8: Conclusions and Discussions

This chapter consists of conclusions drawn from the present studies and discussions on future directions. The future scope of research in supercritical fluid based techniques has been highlighted, which includes measurement of solubility of actinide complexes in SCF medium. This chapter gives a brief outline about the possible outcomes and future directions that could be derived from the present work.

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## ABBREVIATIONS

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<b>Abbreviations</b>	<b>Full name</b>
<b>AARD</b>	Average absolute relative deviation
<b>AcAc</b>	Acetylacetone
<b>AIC</b>	Akaike information criteria
<b>AICc</b>	Corrected Akaike information criteria
<b>BPR</b>	Back pressure regulator
<b>CMPO</b>	<i>n</i> -octylphenyl <i>N,N</i> -di- <i>iso</i> -butylcarbamoylmethyl phosphine oxide
<b>CO<sub>2</sub></b>	Carbon dioxide
<b>D2EHAA</b>	<i>N,N</i> -di-2-ethylhexylacetamide
<b>D2EHIBA</b>	<i>N,N</i> -di-2-ethylhexyl- <i>iso</i> -butyramide
<b>D2EHPVA</b>	<i>N,N</i> -di-2-ethylhexylpivalamide
<b>DAAP</b>	Diamylamyl phosphonate
<b>DBBP</b>	Dibutylbutyl phosphonate
<b>DHDA</b>	<i>N,N</i> -dihexyldecanamide
<b>DHHA</b>	<i>N,N</i> -dihexylhexanamide
<b>DHOA</b>	<i>N,N</i> -dihexyloctanamide
<b>DOHP</b>	Dioctylhydrogen phosphonate
<b>DPO</b>	Dioctylphosphine oxide
<b>HDEHP</b>	Di-(2-ethylhexyl)phosphoric acid
<b>HLLW</b>	High level liquid waste
<b>HPLC</b>	High pressure liquid chromatography
<b>LSC</b>	Liquid scintillation counting
<b>MT</b>	Mendez - Santiago and Teja
<b>P<sub>c</sub></b>	Critical pressure
<b>PC88A</b>	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
<b>RTIL</b>	Room temperature ionic liquid
<b>S</b>	Solubility in g/L
<b>SCCO<sub>2</sub></b>	Supercritical carbon dioxide
<b>SCF</b>	Supercritical fluid
<b>SFC</b>	Supercritical fluid chromatography

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<b>SFE</b>	Supercritical fluid extraction
<b>SSQD</b>	Slow suction quick delivery
<b>TAP</b>	Triamyl phosphate
<b>TBP</b>	Tributyl phosphate
<b>T<sub>c</sub></b>	Critical temperature
<b>TEP</b>	Triethyl phosphate
<b>THP</b>	Trihexyl phosphate
<b>TiAP</b>	Tri- <i>iso</i> -amyl phosphate
<b>TMP</b>	Trimethyl phosphate
<b>TOA</b>	Tri- <i>n</i> -octyl amine
<b>TOMAC</b>	Trioctylmethylammonium chloride
<b>TOMAN</b>	Trioctylmethylammonium nitrate
<b>TOPO</b>	Tri- <i>n</i> -octyl phosphine oxide
<b>TsBP</b>	Tri- <i>sec</i> -butyl phosphate
<b>TTA</b>	Thenoyltrifluoroacetone
<b>y<sub>2</sub></b>	Solubility in mole fraction units

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