**Investigation of the Uranium(VI)-Nitric Acid-Tributyl Phosphate-
Supercritical Carbon Dioxide System**

by

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**Thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of**

Master of Science

Department of Chemistry

**Carleton University
Ottawa, Ontario
June 24, 2006
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ISBN: 978-0-494-18363-2

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Abstract

This work reports on the partitioning of the uranyl ion between nitric acid and supercritical carbon dioxide (scCO₂) in the presence of tributyl phosphate (TBP) as a function of temperature and pressure.

The distribution coefficients (D_U) of uranium (0.2-2.5) were found to be highly dependent on the density of scCO₂. A decrease in D_U was seen to correspond to a decrease in the concentration of TBP in the scCO₂ phase while no corresponding decrease in the concentration of TBP in the aqueous phase was observed.

The system was found to be non-ideal by comparison of the partition coefficients of TBP to the ratio of solubilities of TBP in pure scCO₂ and water.

In the uranium-nitric acid-scCO₂-TBP extraction system, up to 92% of the nitrate in scCO₂ phase was due to the formation and partitioning of the HNO₃TBP complex even though its distribution coefficient is two to three orders of magnitude lower than that of the UO₂(NO₃)₂·2TBP complex.

Acknowledgements

Thank you to Dr. Bob Burk for the use of his lab and equipment, for his guidance throughout this project and excursions on the Shark.

Thank you to Mohamed Abel Salaam, Helen Prochazka, Rana Zoka, Dave Blair, Amber Lemay, Alia Mahabir and Maria Russell for being such a fine lab group.

Thank you to Jim Logan for his electronic expertise; to Tony O'Neil for always being willing to help; to Fred Cassalman for his TA support; to Peter Mosher, Keith Bourque and Wayne Archer for being so friendly; and to Elena, Tanya, Susa and Lisa for always being welcoming at stores and helpful in ordering needed supplies.

Thank you to Dale Robertson for his personal attention to some difficult analyses and the excellent services of Paracel Laboratories; to Dr. DeSilva for his helpfulness and the use of his ICP-ES; to Clem Kazakoff for his MS expertise.

Thank you to my father for his encouragement and support; to my sons Brett, Simon and Lewis for inspiring me with their courage and determination to follow their dreams.

Thank you to Keith C. for impressing upon me the importance of finishing this degree; to Deirdre for her encouragement, receptive ear, espresso machine and last minute computer services; to Janet, Mona, Peggy, and Stuart and all my sailing buddies who were always willing to help restore my equilibrium out on Lac Deschenes.

Thank you to Donna for her encouragement and views on how things look from the supervisor side of the equation.

Thank you to Erika and Bob C. for those training sessions in the Gatineau. There is nothing like climbing up to Pink's Lake a few times on bike or skis to put life back into perspective.

Without your support, this degree would not have been possible.

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1. Introduction

1.1 Supercritical Fluids – Introduction

1.1.1 Historical Background

In 1822 Baron Charles Cagniard de la Tour discovered the phenomenon of the supercritical fluid. He heated substances in the form of liquid and vapor inside a sealed cannon and, rocking the cannon back and forth, discovered that above a certain temperature the sloshing sound disappeared. In order to investigate further he built a glass vessel and observed supercritical fluid for the first time [1] (Figures 1.1-1a, 1.1-1b).

Figure 1.1-1a. Left, two phases of carbon dioxide with meniscus; right, as temperature increases, meniscus is less distinct [2].

Figure 1.1-1b. Left, temperature increases further, gas and liquid densities become closer. Right, “supercritical carbon dioxide” forms one phase [2].

It has been known for over a century that compressed gases, or supercritical fluids, display properties that differ from both liquids and gases and it was thought, even in the early days, that these substances had great potential for chemical applications. The use of water, carbon dioxide and alcohols as supercritical fluids are of particular interest due to the safety, and the low environmental impact and cost of these substances.

1.1.2 Industrial Uses

Decaffeination of coffee and tea, extraction of hops and flavours, and pharmaceutical separations are examples of industrial applications of supercritical fluids presently in use. Due to the unusual properties of supercritical water, it is used to decompose refractory, harmful organics and to depolymerize polymers to monomers and oligomers in the recycling of plastics, etc. Supercritical methanol is used in selective methylation and chemical recycling of waste plastics. Supercritical carbon dioxide can

be used in place of organic solvents in separation techniques, and reaction and material processing [3].

In the 1990s, the U.S. Environmental Protection Agency instituted a voluntary “30-50” program in which a 30% reduction in industrial organic solvent usage was the goal for 1992 with a 50% reduction by 1995 measured against the 1988 toxic release inventory. The program has been expanded to include halons, CFCs, and HCFCs and continues to 2030 [4]. This is a clear indication of the need for a less environmentally-damaging solvent and presents the opportunity for supercritical carbon dioxide to become a more frequently used extraction agent.

From an economic and environmental point of view, large amounts of organic solvents are consumed in the uranium processing industry, reprocessing of spent nuclear fuel, and decontamination of uranium waste. The use of scCO_2 in place of these solvents can minimize purchase and disposal costs since CO_2 is inexpensive, non-toxic, stable under high radiation, and recyclable.

Supercritical fluids have been proposed for remediation of water and soil contaminated by organic compounds. Presently, remediation is performed by distillation, incineration, adsorption and liquid extraction. Soil extraction with supercritical carbon dioxide or ethylene has been shown to remove over 90% of chlorinated aromatics such as PCBs and dioxins.

1.2. Supercritical Fluids – Theory

In the chemical industry the choice of an appropriate solvent is of critical importance and, up until the 1980s, choices were limited to solvents that are liquids at room temperature. At this time it was discovered that the extraction and solvent capabilities of supercritical fluids are controllable through the adjustment of temperature and pressure, and an extensive study of the physical properties of supercritical fluids began. In order to carry out industrial processes accurately, precisely, and economically, the transport properties of supercritical fluids and their solutes must be optimized and the theory behind transport phenomena in dense fluids understood.

A combination of intermolecular attractive forces and the kinetic energy of its molecules determine the state of a fluid – either liquid or gaseous. If the effect of intermolecular forces dominates, the fluid will be in the liquid state whereas, if kinetic energy dominates, the fluid will exist in the gaseous state. In general, as the density of a gas increases (due to higher pressure) the intermolecular effects dominate as the distances between molecules decrease and the fluid condenses. As the temperature increases the kinetic energy of the fluid increases as well and the general tendency is to the formation of a gas. There is a temperature below which condensation to a liquid and evaporation to a gas are possible i.e. the critical temperature, T_c . Above this temperature lies the critical region where only one phase exists - a compressible or a supercritical fluid with properties of both a gas and a liquid. Each substance has its own unique critical temperature [4].

Near the T_c there is a balance between the order imposed by intermolecular forces and the disorder created by the disturbance of these forces by kinetic energy. Thus, at the microscopic level, molecules are changing places rapidly within this overall order and consequently small changes in temperature and pressure result in large changes in average fluid density [3].

1.2.1. Physical Properties of Supercritical Fluids

There are five major physical properties that affect the solubility of substances and their distribution coefficients in supercritical fluids: density, diffusivity, viscosity, polarity and dielectric constant. Table 1.2-1 provides a comparison of three of these properties for gaseous, liquid and supercritical fluids. The supercritical fluid values for these properties lie between those of gases and liquids.

Table 1.2-1. Comparison of density, diffusion coefficient and viscosity of gaseous, liquid and supercritical fluids [5].

	Gases	Supercritical fluids (T_c, P_c), (T_c, $6P_c$)	Liquids
Density (g mL⁻¹)	(0.1-2) 10 ⁻³	0.47 / 1.0	0.6-1.6
Viscosity (g cm⁻¹ s⁻¹)	(1-3) 10 ⁻⁴	3 x 10 ⁻⁴ / 1 x 10 ⁻³	(0.2-3) 10 ⁻²
Diffusion coefficient (cm²/s)	0.1-0.4	7 x 10 ⁻⁴ / 2 x 10 ⁻⁴	(0.2-2) 10 ⁻⁵

Density

Density is important when studying solubility and distribution coefficients in supercritical systems because the dissolving power of a supercritical fluid is strongly dependent on its density. Considering T_c of supercritical carbon dioxide (scCO₂) for example (304 K), as the pressure is increased the properties of carbon dioxide change as it transforms from a liquid-gaseous system at $T < T_c$ to that of a supercritical fluid at $T > T_c$. These properties continue to change as the pressure of the supercritical fluid is increased further. As can be seen in Figure 1.2-1, a small change in pressure in the region of the critical pressure P_c (74 bar) results in a large change in density: at 310 K there is a dramatic increase in density in the region directly above and below P_c (the curve is almost vertical); at 320 K the overall slope is more gradual, but still steep, in the critical region; and at 330 K the near-vertical section of the curve in the critical region has disappeared leaving a curve that does not level out as quickly as the two lower-temperature isotherms.

The concept of the reduced variable is used to study pressure-temperature-density relationships. Dividing the pressure, temperature and volume of a substance by its corresponding critical values (those values present at the critical point of the substance) gives the reduced values

$$P_r = \frac{P}{P_c} \quad T_r = \frac{T}{T_c} \quad \rho_r = \frac{\rho}{\rho_c} \quad (1.2-1)$$

Figure 1.2-1. Density-pressure isotherms at three temperatures for carbon dioxide [1].

(Reproduced with permission.)

where pressure P and density ρ can be expressed in any units, and temperature T is in Kelvin [4]. These critical values can be used to show how density, and therefore solvating power, changes with temperature and pressure. In Figure 1.2-2, the hatched region surrounded by the dark outline (the supercritical fluid region) shows a significant increase in density resulting from a small increase in pressure in the region of $T_r = 1.0-1.2$. A similar change in pressure in the $T_r > 1.6$ shows a remarkably lower change in density with pressure.

Diffusivity

The study of change in solubility with density under supercritical conditions lies in the area of thermodynamics. However, the application of supercritical fluids to industrial processes (with respect to solubility and extraction rates) must also involve the rate of mass transfer, i.e. kinetics, which describes the speed at which the extraction takes place. Diffusion, the transport of a substance down a concentration gradient, affects the rate of mass transfer. The concept of molar flux, $J_{x,1}$, is used to describe diffusion. In the x dimension only, a net number of molecules, δn_1 passes through an area in time δA in δt [1] and the molar flux is

$$J_{x,1} = \frac{\delta n_1}{\delta A \delta t} \quad (1.2-2)$$

in units of $\text{mol m}^{-2}\text{s}^{-1}$. Fick's First Law of diffusion states that flux of a component is proportional to its concentration gradient and, in the x -direction [1]

Figure 1.2-2. Reduced pressure versus reduced density at various reduced temperatures [6]. (Reproduced with permission.)

$$J_{x,1} = -D_1 \frac{dc_1}{dx} \quad (1.2-3)$$

where c_1 is the concentration of component 1 in moles per unit volume, x is the distance, and D_1 is the diffusion coefficient of component 1. The negative sign indicates that the net flux is in the direction of decreasing concentration and the dimensions of the diffusion coefficient are area per unit time, m^2s^{-1} . To accurately describe a fluid, a three dimensional equation is needed. The flux is a vector in the direction of concentration change and equation (1.2-3) becomes [1]

$$J_1 = -D_1 \text{grad } c_1 \quad (1.2-4)$$

As can be seen in Table 1.2-1, diffusion coefficients for supercritical fluids at T_c and P_c are in the range of 10^{-4} compared to liquids which range from 10^{-5} to $10^{-6} m^2s^{-1}$.

According to Taylor, even at high pressures (300-400 atm) diffusivities of supercritical fluids are 1-2 orders of magnitude greater than those of liquids [4]. Figure 1.2-3 shows a comparison of diffusivities of solutes in ordinary liquids and supercritical carbon dioxide. At all temperatures and pressures, solutes have greater diffusivity in supercritical fluids than in ordinary liquids. For the pressure range of 70 to 200 atm, the diffusivity of solutes in supercritical fluids increases with temperature. It can also be seen that over this pressure range, diffusivity decreases as pressure increases. Once again, at higher pressures, an increase in temperature has less effect on density. Also of interest is the

Figure 1.2-3. Diffusivity versus temperature ($^{\circ}\text{C}$) for carbon dioxide, isobars at 70-200 atm [7]. (Reproduced with permission.)

behavior of supercritical carbon dioxide near T_c (31°C): at 70 and 80 atm, a small increase in temperature increases the diffusivity by close to an order of magnitude whereas at higher pressures, greater than 100 atm, the increase in diffusivity is gradual and has no point of inflection.

Viscosity

Although solvent viscosity does not have as great an effect on extraction rates as diffusion, it still plays a part in supercritical extraction and its application to the industrial use of supercritical fluids. Because fluid movement takes place in layers (laminar flow), when supercritical fluid flows into the pressure cell and when stirring is used to decrease the amount of time needed for the system to reach equilibrium, the viscosity becomes relevant. Viscosity is the transport of transverse momentum along a transverse velocity gradient and is always a function of temperature in liquid, gaseous or supercritical fluids [5]. Although pressure does not affect the viscosity of liquids (due to low compressibility) or gases (because the increase in the number of molecules available to transport the momentum is counterbalanced by the shorter mean free path along which to carry it) it has a profound effect on the viscosity of supercritical fluids [5]. Viscosity in supercritical fluids is lower than that of liquids (Tables 1.2-1, 1.2-2) and close to that of gases (Table 1.2-1).

Table 1.2-2. Comparison of density, viscosity and diffusivity of CO₂ (200 atm, 55°C) with three organic solvents at 25°C [4].

	Carbon dioxide (200 atm, 55°C)	<i>n</i>-Hexane (1 atm, 25°C)	Methylene chloride (1 atm, 25°C)	Methanol (1 atm, 25°C)
Density (g mL ⁻¹)	0.746	0.660	1.326	0.791
Viscosity (g cm ⁻¹ s ⁻¹ x 10 ⁷)	1.00	4.45	3.09	6.91
Diffusivity of benzoic acid (m ² s ⁻¹ x 10 ⁹)	6.0	4.0	2.9	1.8

As the viscosity of a solvent increases, the rate of mass transfer of solute decreases. In liquids, there is an exponential decrease in viscosity with increase in temperature [7].

In Figure 1.2-4, at pressures greater than P_c (73 atm) it can be seen that there is a steady increase in viscosity at 77°C as the pressure increases. At lower temperature, 47°C, a small change in pressure results in a large change in viscosity in the region of 100 atm. At even lower temperature (37°C) (but still above T_c) the change in viscosity with a minor change in pressure is substantial.

Figure 1.2-4. Viscosity versus pressure for CO₂ at 37°C, 47°C, 77°C [4]. (Reproduced with permission.)

Polarity

The dipole and quadrupole moments of solute and solvent molecules and the resultant polarities have a substantial effect on solubility, distribution coefficients, and extraction. Polarity is a direct effect of electron cloud imbalance which depends on both inter- and intramolecular interactions.

There are two major forces of attraction to be considered, physical and chemical.

Physical Forces of Attraction

A force of attraction occurs between molecules possessing a permanent dipole resulting from their molecular structure. This dipole-dipole potential energy is expressed as [7]

$$\Gamma_{ij} = -C_2 \frac{\mu_i^2 \mu_j^2}{r^6 kT} \quad (1.2-6)$$

where μ is the strength of the dipole in Debye (D), T is the temperature in Kelvins, k is Boltzman's constant, r is the distance between molecules, and C_2 is a constant. This is a short-range force, and is dependent on temperature. Interactions increase with a decrease in temperature since lower thermal energy allows the molecules to better align. In this case, the dipole moment is the most significant parameter and has a substantial effect if the magnitude is larger than one Debye [7].

A second intermolecular force resulting from interactions between molecules, the quadrupole moment, is present in supercritical carbon dioxide. The solvent-solvent intermolecular energy resulting from this interaction is expressed as [7]

$$\Gamma_{ij} \approx -C_3 \frac{Q_i^2 Q_j^2}{r^{10} kT} \quad (1.2-7)$$

where Q is the quadrupole moment, r is the distance between molecules i and j , k is Boltzmann's constant, T is the temperature in Kelvin and C_3 is a constant. Since the potential energy is inversely proportional to r^{10} , this force falls off rapidly as r increases. Thus the force of attraction is closely based on r and has a great effect on solubility. Dipole-quadrupole interactions follow the potential energy equation [7]

$$\Gamma_{ij} = -C_4 \frac{\mu_i^2 Q_j^2}{r^8 kT} - C_5 \frac{\mu_j^2 Q_i^2}{r^8 kT} \quad (1.2-8)$$

where Q is the quadrupole moment, μ is the strength of the dipole in Debye, r is the distance between molecules i and j , k is Boltzmann's constant, T is the temperature in Kelvin and C_4 and C_5 are constants.

To determine whether a solute will dissolve in a particular solvent, the net effect of intermolecular forces between solvent-solvent, solute-solute, and solvent-solute must be considered. The interchange energy, E , of mixing of molecular pairs i and j is described by the following equation [7]

$$E = z \left[\Gamma_{ij} - \frac{1}{2} (\Gamma_{ii} + \Gamma_{jj}) \right] \quad (1.2-9)$$

where z is the number of dissimilar solvent-segment pairs in solution. In order for a solute to dissolve, the sum of the like-like interactions of the solute and solvent, Γ_{ii} and Γ_{jj} must be less than the unlike interactions, Γ_{ij} . Equations (1.2-6-1.2-9) do not hold true at very high pressure, i.e. high density, because under this condition repulsive interactions become large and outweigh the attractive forces. This explains why, under high pressure conditions, solubility decreases with increasing pressure.

Table 1.2-3 lists the dipole moments of some of the most common compounds used as supercritical fluids. It is interesting to note that according to Shoenmakers [9], the polarity of a solvent is better described by its solubility parameter than by its dipole moment or dielectric constant. The solubility parameter, a first approximation for the solvating power of a particular substance, is calculated as the square root of the cohesive energy (the energy content E , cal/mol) of the fluid per unit molar volume (cm^3/mol) relative to its ideal gas state [4]. Table 1.2-3 also lists solubility parameters based on the Lee and Kessler equation of state. As can be seen in Table 1.2-3, there is no correlation between the dipole moment and the solubility parameter under supercritical conditions [9].

Table 1.2-3. Permanent dipole moment and solubility parameter of some commonly used supercritical fluids [4,5].

Supercritical fluid	Dipole moment (Debye) [5]	Solubility parameter δ at $T_r=1.02$, $P_r=2$ [4]
Carbon dioxide	0.0	7.5
Sulfur hexafluoride	0.0	5.5
Xenon	0.0	6.1
Ethane	0.0	5.8
<i>n</i> -butane	0.0	5.3
Nitrous Oxide	0.2	7.2
Freon-12	0.2	
Freon-11	0.5	
Freon-22	1.4	
Ammonia	1.5	9.3
Fluoroform	1.6	
Methanol	1.7	
Water [11]	1.854	

According to Lague de Castro, those substances with dipole moments less than 1.4 Debye are useful for dissolving non-polar and slightly polar solutes [5]. Solutes of high polarity require solvents such as ammonia, fluoroform or methanol. The difficulties of working with these highly polar solvents (toxicity, cost, corrosiveness, reactivity, etc.) have led chemists to add modifiers (compounds that modify the polarity of the solvent

e.g. methanol) to less polar supercritical fluids to make them suitable solvents for work with polar solutes. Another option when trying to extract polar solutes into solvents of low polarity is to use a complexing agent and/or counter ions to decrease the polarity or neutralize the charge of the solute.

Chemical Forces of Attraction

Included in chemical forces of attraction are hydrogen bonding and electron donor-acceptor complexation. Chemical forces differ from physical forces in that chemical forces become saturated whereas physical forces do not. Each molecule has a fixed number of sites available for hydrogen bonding or ligand-metal bonding and, once these sites have formed bonds, no other sites will become available without first breaking the original bonds. Chemical forces are more dependent on temperature than are physical forces. In the case of hydrogen bonding for example, as the temperature increases, the precise alignment required for hydrogen bonding to take place becomes less likely as molecular motion increases.

Dielectric Constant

The dielectric constant of a solvent is a measure of the response of the charge on its molecules to an external electric field [10]. This charge is based on the dipole moment of its molecules, i.e. the imbalance in electron cloud due to differences in electronegativities of the atoms. Two supercritical fluids, water and ammonia, have high

dipole moments, 1.854 D and 1.5 D respectively (Table 1.2-3) and also have high dielectric constants, 80.1 and 16.61 (as compared to a vacuum with a value of 1) [11]. These solvents are therefore suitable for polar and ionic solutes. They are, however, poor solvents for non-polar solutes since the only attractive forces present between the nonpolar solute molecules and the polar solvent molecules are weak dipole induced-dipole forces. Carbon dioxide on the other hand has a dipole moment of 0.0 and corresponding dielectric constant of 1.4492 [11] making it a non-polar solvent suitable only for dissolving non-polar solutes.

Pressure has a pronounced effect on the dielectric constant of some supercritical fluids as can be seen in Figure 1.2-5. According to Russell, fluoroform has the physical properties of propane at 600 psi and of methylene chloride at 4000 psi [12]. Table 1.2-4 shows the effect of pressure and temperature on the dielectric constant of supercritical water. This variability in dielectric constant allows the properties of the solvent to be tuned to a particular solute, to the extent that one solute may be selectively extracted in the presence of contaminants. In the case of a solution of different metals, the metal of interest may be extracted leaving the other metals in solution or, conversely, the extraneous metals may be extracted leaving the metal of interest in solution.

Figure 1.2-5. Response of dielectric constant to pressure for sulfur hexafluoride (1), fluoroform (2), propane (3), and ethane (4) at 50°C [12]. (Reproduced with permission.)

Table 1.2-4. Effect of pressure and temperature on dielectric constant of supercritical water [1].

Temperature(°C)	300 bar	400 bar	500 bar
0	89.2	89.6	90.1
100	56.4	56.8	57.1
200	35.9	36.3	36.6
300	22.0	22.6	23.1
400	6.0	10.5	12.2
500	1.7	2.3	3.4

1.2.2. Gibbs Phase Rule

In order to discuss a system at equilibrium, it is necessary to know the number of intensive variables (those which are independent of the size of the system e.g. temperature, pressure, density, concentration) required to define its thermodynamic state. The number of intensive variables is referred to as the number of degrees of freedom.

The Gibbs Phase Rule relates the number of phases present at equilibrium to the number of components at specified composition x , temperature T and pressure P . Thus, the number of degrees of freedom of the system becomes:

$$F = c + 2 - p \quad (1.2-10)$$

where F is the number of degrees of freedom, c is the number of components and p is the number of phases.

A binary mixture results when a second component is dissolved in a supercritical fluid. This second component may act as a modifier, for example the addition of methanol to a non-polar supercritical fluid to improve its solvent capability for more polar solutes, or it may act as a ligand, for example tributyl phosphate as a complexing agent to enable partitioning of metal ions from aqueous to non-polar supercritical fluid phase.

The number of independent intensive variables required to describe the state of a binary two-component one-phase system is three. If temperature, pressure and one composition (the mole fraction of one component) are chosen, all equilibrium states of the system can be described in a three-dimensional $P - T - x$ space. [7].

1.2.3. Solubility of Solids and Liquids in Supercritical Fluids

The solubility of relatively large, high molecular weight compounds is described in Figure 1.2-6. The solid line indicates solubility at low pressures and the dashed lines possible solubilities at higher pressures. A represents the vapour pressure of the solute with no solvent present. The initial fall at low pressures, AB , corresponds to dilution of the solute as solvent is added. Moving along the x -axis to the right, as solvent is added the solute is diluted with little solvation taking place due to low density of the supercritical phase. Progressing to C , solvation increases as the density of the solvent increases and shorter distances between solute and solvent molecules allow short-range attractive forces to come into play. The solubility increases most rapidly in the region of critical density. Looking at the dashed lines from C to D , E and F , CD shows that

Figure 1.2-6. Solubility trend in a supercritical fluid with pressure at constant temperature [1]. Points A-E are defined in the text. (Reproduced with permission.)

maximum solubility was reached at *C* and remains constant. *CE* shows a decrease in solubility of the solute as the density of the supercritical fluid increases and repulsive solute-solvent interactions take place due to the close proximity of the molecules. The increase at *CF* is based on the presence of a critical line at high pressure at the temperature of the isotherm. When the pressure is held constant and the temperature changed, the solubility behavior seen in Figure 1.2-7 occurs. This trend in solubility with temperature change is based on the vapour pressure of the solute and the ability of the solvent to solvate the solute, based on the density of the solvent. The decrease at lower temperature shows the inability of the rising vapour pressure to compensate for the decreasing density as the temperature increases. With continued temperature increase, the effect of the increasing vapour pressure overcomes the increasing inability of the supercritical fluid to solvate as the density decreases even more. Not all compounds show the full range decrease, minimum and maximum.

1.2.4. Thermodynamics of Solubility

Based on the Gibbs-Helmholtz equation

$$\Delta G = \Delta H - T\Delta S \quad (1.2-14)$$

when ΔG (the free energy of mixing) is negative, dissolution will take place. ΔS (the entropy of mixing) is usually large so ΔH (the heat of mixing) determines the solubility of a solute [5]. Hildebrand defines the heat of mixing as [5]

Figure 1.2-7. Solubility trend in a supercritical fluid with temperature at constant pressure [1]. (Reproduced with permission.)

$$\Delta H = v_1 v_2 (\delta_1 - \delta_2)^2 \quad (1.2-15)$$

where ΔH is the energy change from the breakage and formation of intermolecular bonds, v_1 and v_2 are the partial volumes of the solvent and solute respectively, and δ_1 and δ_2 are the solubility parameters of the solvent and solute respectively. Therefore, it is the difference between the solubility parameters that determines the solubility. For solubility to take place, the attraction of the solvent molecules for the solute molecules must overcome the cohesion energy of the crystal structure of the solute. The solubility of the solute is described by its solubility parameter [5]

$$\delta = \sqrt{\frac{\Delta E_v}{v}} = \sqrt{\frac{\rho(\Delta H_v - RT)}{M}} \quad (1.2-16)$$

where ΔE_v is the vaporization energy, v is the molar volume, ρ is the molar density, ΔH_v is the heat of vaporization, R is the gas constant, T is the temperature in Kelvin, and M is the molecular weight of the solute. The solubility parameter for a supercritical fluid is described by Giddings as [5]

$$\delta_1 = 1.25 \sqrt{P_c} \frac{P_{r,SF}}{P_{r,L}} \quad (1.2-17)$$

where P_c is the critical pressure, $\rho_{r,SF}$ is the reduced density of the supercritical fluid, $\rho_{r,L}$ is the reduced density of that fluid in the liquid state. Equation (1.2-17) shows the dependence of the solvent power of the supercritical fluid on its density. Figure 1.2-8 shows the effect that pressure has on the solubility parameter of some supercritical fluids, the greatest effect being in the region at, and immediately above the P_c .

Temperature, especially at high pressures, has a significant effect on solubility parameter and Figure 1.2-9 shows the change in solubility parameter with temperature for various isobars of nitrous oxide [5].

1.3. Supercritical Carbon Dioxide

Supercritical carbon dioxide offers many advantages over conventional solvents for the extraction and separation of compounds from liquid and solid samples. The extraction efficiency is enhanced due to the rapid mass transfer of solute in $scCO_2$. Gasification of the $scCO_2$ after extraction provides an easy and efficient method of separation of extracted substances. The low viscosity of $scCO_2$ makes it an ideal solvent for the removal of contaminants from solid materials for environmental monitoring and remediation processes. Also, the solvent properties of $scCO_2$ can be widely varied and thus optimized by tuning the temperature and pressure of the extraction system allowing high selectivity.

Figure 1.2-8. Pressure variation of solubility parameter for some common supercritical fluids. P_c is the critical pressure [7]. (Reproduced with permission.)

Figure 1.2-9. Effect of temperature on solubility parameter for isobars (atm) of supercritical nitrous oxide. T_c is the critical temperature [7]. (Reproduced with permission.)

1.3.1. Phase Diagram of Carbon Dioxide

The critical parameters of carbon dioxide are $T_c = 31^\circ\text{C}$ and $P_c = 74$ bar. The phase diagram in Figure 1.3-1 shows the states of CO_2 under various temperature and pressure conditions. Three phases, solid, liquid and gas, are divided by solid lines that also represent equilibrium conditions between the two adjacent states e.g. the liquid-solid line between the triple point TP and the critical point CP represents the vapour pressure of CO_2 . To the right of the CP lies the supercritical region. This diagram defines a supercritical fluid as a substance that is above its critical temperature T_c and above its critical pressure P_c . Thus T_c is the highest temperature at which an increase in pressure will transform a substance from the gaseous to the liquid state and P_c is the highest pressure at which a liquid can be converted to a gas by an increase in the temperature of the liquid [7].

1.3.2. Carbon Dioxide/Water System

1.3.2.1. Effect of Carbon Dioxide on pH of Aqueous Phase with Change of Temperature and Pressure

Carbon dioxide dissolves in water with the concentration of CO_2 in the water increasing as the pressure increases (Henry's Law) according to the following equations.

Figure 1.3-1. Pressure-temperature projection of the phase diagram for CO₂ showing isobars for 100-1200 g L⁻¹. *CP* is the critical point, *P_c*, the critical pressure, *T_c* the critical temperature [13].

At temperatures of 25-70°C and pressures of 70-200 atm, dissolution of CO₂ in water results in a decrease in the pH of water to values of 2.80 to 2.95 [14]. However, in a system where the aqueous phase has been initially acidified to pH 0 or below (experimental conditions used in this thesis), the first and second dissociation constants of carbonic acid ($K_1 = 4.5 \times 10^{-7}$, $K_2 = 4.7 \times 10^{-11}$ at 25°C and 1 atm) dictate that the carbonic acid equilibrium will lie heavily to the left in equation (1.3-3) and therefore will not have a significant effect on the pH of the aqueous phase. Although the K_1 has been shown to increase with pressure (by a factor of ten up to 3000 atm) [15] no effect will be seen at pH 0 or below. An increase in temperature from 25-250°C shows a tenfold decrease in K_1 [16] and will therefore have no significant effect on the pH at 0 or below either.

1.3.2.2. Effect of Water on Supercritical Carbon Dioxide Phase

When performing extractions from aqueous to scCO₂ phases, in addition to CO₂ dissolving in the aqueous phase, water also dissolves in the scCO₂ phase. According to King *et al*, over the range of 40-100°C and 50-700 atm water dissolves in scCO₂ in quantities ranging from 0.00222-0.577 mole fraction [17]. The presence of water in the scCO₂ phase has been shown to enhance the

distribution of metal complexes [20,21].

1.3.3. Solubilities in Supercritical Carbon Dioxide

The solubilities of solids and liquids in scCO_2 may be determined through dynamic or static methods. In the dynamic method, after placing the compound into the extraction cell, a steady stream of supercritical fluid is passed over or through the solute. The saturated fluid leaves the cell and is decompressed, allowing the solute to be measured. The flow rate must be measured and must be low enough that the equilibrium of the cell is not disturbed during the collection process.

In the static method, the solute is placed into the cell which is then sealed and charged with the supercritical fluid. Time is allowed for equilibrium to be reached and a sample is withdrawn. The sample is removed quickly to minimize disturbance of equilibrium. A pre-determined amount of time is allowed to elapse before the cell is sampled again to ensure that equilibrium has been re-established.

In both methods, the temperature and pressure must be kept constant to ensure that the density of the scCO_2 does not vary. Also, a system of rinsing residual solute from the collection system must be in place to ensure complete sample collection and no carryover between samples.

1.3.3.1. Case Study – Naphthalene

The increase in solubility of a solid at temperatures above T_c illustrates the change in solvent properties of scCO_2 with temperature and pressure or, more accurately,

density. Figure 1.3-2 shows the solubility of naphthalene in supercritical CO₂ as a function of temperature. At high pressures (150-300 bar), and thus high densities, the solubility of naphthalene increases with increasing temperature in a predictable manner, but at 100 bar an unexpected trend is observed: as the temperature increases the solubility decreases. It is expected that with increasing temperatures, the density of the scCO₂ would decrease and thus the solubility of naphthalene would decrease accordingly but Figure 1.3-2 (except at 100 bar) indicates an opposite trend. Figure 1.3-3, solubility of naphthalene versus density, shows that at constant temperature, solubility increases with increasing density. Figures 1.3-2 and 1.3-3 show that the pressure-temperature-density relationship under supercritical conditions is not a straightforward one. In fact, the density decreases markedly with an increase in temperature at low pressure (which explains the decreasing solubility of naphthalene with increasing temperature at 100 bar) but at higher pressures an increase in temperature has much less effect on density. Therefore plotting solvent power, extraction efficiency, distribution coefficients, etc. versus temperature or pressure is analogous to comparing apples and oranges since a supercritical fluid has different properties at different temperatures and pressures (see isobars in Figure 1.3-1). To overcome this confusion, throughout this thesis, density, not temperature or pressure, will be used as the independent variable as required. (See Appendix 1 for pressure, temperature, density data.)

The pressure-temperature-density relationship is illustrated by Figure 1.3-4 and shows the change in solubility of solid naphthalene in supercritical ethylene with increasing pressure at two temperatures, 12°C and 35°C. Given that the critical

Figure 1.3-2. Solubility of naphthalene in scCO₂ versus temperature at 100-300 bar [13].

(Reproduced with permission.)

Figure 1.3-3. Solubility of naphthalene versus density in carbon dioxide at $T = 35, 45, 55^{\circ}\text{C}$ [13]. (Reproduced with permission.)

Figure 1.3-4. Solubility of naphthalene versus pressure in ethylene at 12°C and 35°C.

T_c ethylene = 9.3°C [7]. (Reproduced with permission.)

parameters of ethylene are $T_c = 9.3^\circ\text{C}$ and $P_c = 49.8 \text{ atm}$, in the region near 50 atm, it is expected that an increase in pressure (and therefore density) would have a greater effect at a lower temperature than at a higher temperature. Figure 1.3-4 shows that the change in density, i.e. solvent power, is more dramatic at 12°C than at 35°C in the region of the critical pressure (49.8 atm). Up to 100 atm, naphthalene is more soluble at 12°C than at 35°C . If the reader compares the T_r parameters at 12°C ($T_r = 1.01$) and 35°C ($T_r = 1.09$) of ethylene to Figure 1.2-2, it can be seen that, as expected, at $T_r = 1.01$ (12°C) the solubility is more sensitive to a change in pressure in the supercritical region than at $T_r = 1.09$ (35°C) [4]. The lower solubility of naphthalene at 35°C than at 12°C at pressures less than 100 atm is due to the lower density of ethylene at higher temperatures. The higher solubility of naphthalene above 100 atm at higher temperatures is thought to be due to the higher vapour pressure of naphthalene at higher temperatures and is unrelated to the density of the solvent [4]. At pressures above 150 atm, little change in solubility is seen at high or low temperature as was explained above.

1.4. Extraction

When extracting polar or charged species from an aqueous to a non-polar solvent, a chelating agent can be used to enhance the extraction. The solubility of the chelating agent in the organic phase affects the distribution coefficient of the agent.

1.4.1. Thermodynamics of Solubility

The enthalpy of solution of a solute in a solvent gives an indication of the energy released and absorbed as a solute establishes distribution equilibrium.

$$K_{\text{eq}} = \frac{[\text{solute}]_{\text{solution}}}{[\text{solute}]_{\text{solid}}} = \frac{a_{\text{solute, solution}}}{a_{\text{solute, solid}}} \quad (1.4-2)$$

where a is the activity of the solute, with the assumption that

$[\text{solute}]_{\text{solution}} = a_{\text{solute, solution}}$ and since $a_{\text{solute, solid}}$ is, by definition, equal to 1, it follows that

$$K_{\text{equilibrium}} = [\text{solute}]_{\text{solution}}$$

$\Delta H_{\text{solution}}$ can then be calculated from the slope of the curve in $\log K$ versus $1/T$ and

$\Delta S_{\text{solution}}$ can be found from the intercept.

Since

$$\Delta G = -RT \ln K \quad (1.4-3)$$

$$\Delta G = \Delta H - T \Delta S \quad (1.4-4)$$

$$\Delta H - T \Delta S = -RT \ln K \quad (1.4-5)$$

$$\ln K = \frac{-\Delta H}{R} \left(\frac{1}{T} \right) + \frac{\Delta S}{R} \quad (1.4-6)$$

$$\text{slope} = \frac{-\Delta H}{R} \quad \text{intercept} = \frac{\Delta S}{R}$$

$$\Delta H = -\text{slope} \cdot R \quad (1.4-7)$$

$$\Delta S = \text{intercept} \cdot R \quad (1.4-8)$$

Depending on the amount of energy required to break the solute-solute bonds and the energy given off by the formation of the solvent-solute bonds, the enthalpy and entropy of solution can be positive or negative i.e. an exo- or endothermic reaction.

1.4.1.1. Liquid-liquid Extraction

Many of the principles of liquid-liquid extraction are applicable to supercritical extraction since, in both cases, two immiscible solvents are brought into contact with each other in order to transfer one or more solutes to the second solvent.

The partition or distribution coefficient, D , is defined as the ratio of the concentration of the analyte between two immiscible solvents. Equation (1.4-9) is valid as long as the activity of the solute is close to its concentration, and the solute does not interact with other species present in either phase, or the solvents themselves.

$$D = \frac{[\text{analyte}]_o}{[\text{analyte}]_w} \quad (1.4-9)$$

The equation for the percent extraction from aqueous to organic phase indicates that the volume ratio as well as D influences the efficiency of the extraction [18]

$$E \equiv \frac{100[A]_o V_o}{[A]_o V_o + [A]_w V_w} = \frac{100D}{D + V_w/V_o} \quad (1.4-10)$$

where V_o represents the volume of the extracting solvent, A is the analyte and subscripts w and o represent the aqueous and organic phases respectively. In cases where there is little chemical interference (from other species in solution) in either phase, the ratio of solubilities of the analyte in each phase may be used to approximate the distribution coefficient. Hildebrand's Theory of Regular Solutions states that, in the absence of chemical interferences, as the solubility parameter (δ) of solute and solvent approach each other, the solubility increases. The solubility parameter, as defined by Hildebrand, is the square root of the heat of vaporization per mL and is a measure of the cohesive energy density [18].

Pasquinelli correlated mutual solubilities of liquids using dipole moments, dielectric constants, specific magnetic susceptibility, and molar volume to within $\pm 3\%$ [18].

1.4.1.2. Supercritical Carbon Dioxide Extraction

1.4.1.2.1. Effects of Temperature, Pressure, and pH

Changing the density of an aqueous-scCO₂ system is achieved by adjusting the temperature and pressure. Because water is a non-compressible fluid, changes in pressure have little effect on the solvation properties of the aqueous phase. However, changes in pressure have a substantial effect on the solvation properties of scCO₂. At low densities there are inadequate numbers of CO₂ molecules to solvate the solute. As the density increases, CO₂ becomes a better solvent and, as it approaches the critical density of 0.47 g mL⁻¹, the density changes rapidly and therefore substantial changes are seen in the solvation properties as well. At very high pressures of CO₂ (in the range of 0.8-0.9 g mL⁻¹) solute and solvent molecules are in such close proximity that repulsive electronic forces reduce solvation.

Temperature affects the partial pressure of solutes dissolved in the aqueous phase. In the case of complexing agents used for metal extraction, temperature can be an important influence on the partition coefficient of the complexing agent and therefore on the distribution coefficient of the metal complex as well.

The pH of the aqueous phase has a direct effect on the partitioning of metal species to the scCO₂ phase because the degree of dissociation of the complexing agent affects its ability to complex with a metal cation and the metal ion itself may be acidic or basic. pH can affect the partitioning in two ways. If the pH is high enough that the complexing agent will be deprotonated, the metal cation is more likely to bind to the

negatively charged agent. However, at high pH (3.5-4.0) the metal ion can hydrolyze and precipitate out of solution. If the complexing agent contains amine groups, at low pH they become protonated and cannot bind with metal cations.

1.4.2. Complexation and Extraction of Uranium

1.4.2.1. Agents Used for Complexation of Uranium

1.4.2.1.1. Crown Ethers and Synergists

Crown ethers have the ability to form complexes with metal ions and offer selectivity based on the size of the ring cavity. The relationship between the radius of the ion and the cavity size is of importance as is the type of donor atoms in the ring. The extent of extraction of uranium by crown ethers has been linked to crown ether basicity, steric factors, and the number of ether oxygen atoms available to bind the cation [27]. Although benzyl additions to the ring make the complex amenable to detection by UV-Visible absorption spectroscopy, and benzyl and cyclohexyl substituents make the complex more soluble in non-polar solvents, both these substituents have the disadvantage of increasing the rigidity of the ring and, in the case of benzyl substituents, reducing the basicity of the ring due to their electron-withdrawing nature [22].

Since metal extraction with crown ethers may be enhanced by the presence of a counter ion, another important consideration is the dielectric constant of the solvent into which the metal ion complex is extracted [23,22]. If the diluent has a low dielectric

constant (e.g. chloroform, benzene), association of the ion pairs is enhanced whereas, in a diluent with a high dielectric constant, nitrobenzene for example, there will be strong interactive forces between the oxygen atoms of the crown and the hydrogen atoms of the diluent resulting in interference with the association of the ion pairs [23].

Although nitrate is a commonly used inorganic anion in industrial metal extraction processes [22], fluorinated compounds have been found to increase extraction efficiency and they are more soluble in scCO_2 than hydrocarbons of a similar nature. One theory proposes that this increase in solubility is due to the highly repulsive nature of fluorocarbon-fluorocarbon interactions resulting in less favourable solvent-solvent interactions and more favourable solvent-solute interactions [24]. A second theory postulates that the enhanced solubility of fluorinated compounds in scCO_2 is related to interactions of the electron-rich fluorines in the C-F bonds with the relatively electron-poor carbon in the CO_2 molecules [25]. Additionally, the acidity of these molecules is improved by the strong electron withdrawing nature of the fluorinated tail. [24,26,27,28].

The molecular structures of crown ethers and the synergist used in this research can be seen in Figure 1.3-5.

1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane (2N)

Dibenzo-24-crown-8
(DB24C8)

Dicyclohexano-24-crown-8
(DC24C8)

18-crown-6
(18C6)

Dicyclohexano-18-crown-6
(DC18C6)

Perfluoro-1-octanesulfonic Acid, Tetraethylammonium Salt (PFOSA)

Figure 1.3-5. Molecular structures of crown ethers and synergist.

1.4.2.1.1.1. Literature Review of Extraction of Uranium with Crown Ethers and Synergists

Uranium extraction into toluene and chloroform using DC18C6 and DB24C8 was carried out by Shukla *et al* [22]. Uranium and plutonium were extracted into chloroform, dichloromethane, and toluene with DC18C6, DB24C8, DB18C6 [22]. Uranium was extracted with DB24C8 from HCl [29] and from hydrobromic acid with DB24C8 [36] into nitrobenzene. DC18C6 (isomer A cis-syn-cis, and isomer B cis-anti-cis) was used to

extract uranium from HCl solution into 1,2-dichloroethane [31,32] and (isomers not identified) to extract uranium with nitrate as counter ion into paraffinic and halogenated solvents [26]. DB24C8 was used to extract uranium into nitrobenzene and 1,2-dichloroethane [33].

DC18C6 was used to extract strontium to scCO_2 [34] and was also used in combination with fluorinated counter ions PFOA (perfluorooctane-1-sulfonic acid, tetraethylammonium salt) and PFOSA (pentedecafluorooctanoic acid) [26,34]. Extraction of strontium has been carried out in scCO_2 using DC18C6, with synergists PFOA and PFOSA [34]. The extraction efficiency of cesium, potassium and sodium with DB24C8, DC18C6 and 18C6 into scCO_2 was seen to increase with the addition of fluorinated counter ions PFOA and PFOSA [35]. 18C6 with PFOA was used to extract alkali metals into scCO_2 [36].

1.4.2.1.2. Calixarene

Calixarenes are composed of phenolic groups joined by methylene bridges. The phenolic groups are free to rotate around the methylene bridges thus forming a “cup” with potential substituent binding sites on the upper and lower “rims”. The polar lower “rim” allows the calixarene to form inclusion complexes with metal ions, and the upper non-polar “rim” allows the complex to dissolve in non-polar solvents. Calixarenes with non-polar substituents, e.g. *tertbutyl*, have been synthesized to increase their solubility in non-polar solvents. When complexing with calix[6]arene, the uranyl ion forms a pseudo-planar penta- or hexa-co-ordinate structure with the oxygen atoms of the uranyl ion [37].

Ramkumar *et al* found that the amount of uranyl ion transported to CHCl_3 by calixarene was pH dependent, with a greater percentage of the uranium transported as the pH increased. They suggest that this may be evidence of ion exchange and, at lower pH, equilibrium favours protonation of the alcoholic substituents thus preventing complexation with the uranyl ion [37]. In view of this lower limit on the pH, finding an appropriate pH at which to extract uranium with calixarenes becomes a balancing act because hydrolysis of the uranyl ion occurs at $\text{pH} > 3.5 - 4.0$.

Below is the molecular structure of the calix[6]arene used in this research.

Figure 1.3-6. Calix[6]arene in 2-D and Calix[4]arene in 3-D (showing only 4 of the 6 phenolic units for clarity).

1.4.2.1.2.1. Literature Review of Extraction of Uranium with Calixarene

A report by the U.S. Department of Energy refers to calix[6]arene as a barrel-shaped “super-uranophile” [38]. Calix[6]arene has been used to extract uranium into chloroform with tri-*n*-octyl phosphine oxide (TOPO) [37]. Calix[6]arene-*p*-

hexasulfonate successfully extracted uranium and it was determined that the sulfonate groups were not responsible for uranyl ion binding [39].

1.4.2.1.3. Tributyl Phosphate

Extraction of metals into non-polar solvents such as scCO_2 with any measurable efficiency requires neutralization using a suitable counter-ion, and often complexation with a suitable organic ligand. Tributyl phosphate is used in solvent extraction for the recovery of uranium from irradiated nuclear fuel.

Tributyl Phosphate (TBP)

Figure 1.3-7. Molecular structure of tributyl phosphate.

TBP is also widely used in the extraction process of uranium from ore (30 volume % in hydrocarbon diluent – dodecane, kerosene). For these reasons TBP was chosen as the complexing agent for uranium in this research project with the counter ion, NO_3^- , supplied by the nitric acid in the aqueous phase.

TBP is a large polar basic, non-electrolyte with highly-local specificity for one water molecule. It has low solubility in water, approximately 422 mg L^{-1} at 25°C and the solubility increases as the temperature decreases (1075 mg L^{-1} at 3.4°C) [40]. A

molecular dynamics study done by Baadan *et al* [41] suggests that the role of TBP in the scCO₂-nitric acid system is to reduce interfacial tension between the two phases allowing the charged uranyl ion to approach the interface of the non-polar scCO₂. At this point it is complexed with the TBP and crosses the phase boundary embedded in the overall hydrophobic complex, having formed a neutral ion pair with two nitrate anions.

According to Ritcey *et al*, the mechanism of extraction with organophosphorous compounds is the formation of a coordination bond between the oxygen of the phosphoryl group and the metal. The strongly polar TBP replaces the water molecules in the primary coordination sphere of the metal ion [90].

TBP also reacts with nitric acid to form a hydrogen-bonded complex, HNO₃TBP, that is highly soluble in scCO₂ and provides a method of introducing nitric acid to the scCO₂ for the dissolution of solid UO₂ in the reprocessing of spent nuclear fuels and treatment of nuclear waste [42].

1.4.2.2. Literature Review of Extraction of Uranium

Research on the extraction of uranium has been on-going for decades and there are numerous journal articles on this topic. The literature therefore has been classified as simply as possible under general headings. Many of the articles belong under more than one heading but for brevity, they appear once only. References found in the body of this thesis are not re-recorded in this section.

Historical Early Work

One of the early papers [1998] was written by Carrott *et al* reporting the high solubility of the TBP-uranyl complex in scCO₂ at modest temperatures and pressures, and the potential of this method to replace the organic solvents used in nuclear fuel processing [78]. Toews *et al* reported on the extraction of uranyl nitrate with organophosphorous ligands and scCO₂. Among TBP, TOPO, and tri-phenyl phosphine oxide (TPO), TBP formed the most stable complex with excellent transport capabilities. TOPO and TPO complexed well but were difficult to transport (probably due to solubility limitations). There was no secondary phase formation observed with TBP [79]. Iso *et al* reported a selective extraction method for uranium using scCO₂ and a hydrophobic organic complexing agent [80]. Wai *et al* extracted metal species from solid and liquid material to scCO₂ with dithiocarbamates, β -diketones, organophosphorus reagents and macrocyclic compounds for metal recovery and mineral processing [81]. Kawasaki described a method of recovery of TBP and diluent using scCO₂. The TBP-diluent solution containing decomposition products was first contacted with scCO₂ to separate the TBP-diluent from the decomposition products, then the pressure was decreased to below critical pressure to separate the organic solvent from the CO₂ [82]. Smart *et al* used TBP and phosphine oxides in scCO₂ to extract U(VI) and Th(IV). The process was found to be similar to conventional extraction systems i.e. extraction efficiency with TBP increased with increasing acidity. The solubility of ligands in scCO₂ was examined [83]. An early patent [1995] was taken out by Wai for removing contaminants from industrial waste, especially actinides and lanthanides from acidic solution using trialkyl phosphate,

a triaryl phosphate, an aralkyl phosphate, a trialkylphosphine oxide, a triarylphosphine oxide, an aralkylphosphine oxide and mixtures of these [84]. Iso reports the extraction of U(VI) to scCO_2 containing 3% TBP at 60°C and 148-345 atm with rapid removal of the CO_2 medium by gasification at atmospheric temperature and pressure [85]. Furton *et al* extracted uranyl nitrate using methanol-modified scCO_2 and 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octadione (FOD), TBP and ethanol from solid matrices polypropylene/polyester, glass wool, cotton, clay. In comparison to liquid extraction, scCO_2 yielded higher recoveries, was faster, had equal or greater precision than liquid extraction, and greatly reduced the quantity of organic solvent used. UV absorption was used for detection and was found to be linear over three orders of magnitude (ppb-ppm) [86]. Lin *et al* extracted thorium and uranium from mine waters and mine water-contaminated soil using methanol-modified scCO_2 and a fluorinated β -diketone at 60°C and 150 atm. Extraction was also successful in scCO_2 -TBP solution with a fluorinated β -diketone [59].

Dissolving and Reprocessing of Spent Wastes

Wai extracted cesium, strontium, and uranium from solid and liquid matrices to scCO_2 using fluorinated and phosphorous-containing ligands. Uranium was extracted as the uranyl-beta-diketone-TBP complex and the uranyl-TBP-nitrate complex. Extractions were performed using neither acid nor solvent [43]. Meguro *et al* [44] used supercritical fluid leaching, and Shimada *et al* used a “direct extraction column” (Super-DIREX) [45] in the decontamination process of radioactive wastes using scCO_2 , TBP and HNO_3 to

separate uranium and plutonium [46]. Miyaki *et al* extracted uranium and plutonium from spent nuclear fuel using TBP and scCO₂ [47]. Enokida *et al* used TBP to extract uranium from solid UO₂ with scCO₂ [43]. Fujioka *et al* invented an extraction process whereby CO₂, TBP, gaseous HNO₃ and nuclear fuels are fed into an extraction vessel and reacted. Uranyl and plutonium complexes are dissolved into the scCO₂ and collected. Fission products that do not form TBP complexes and insoluble residues are discharged and separated [48]. Wai *et al* reported the removal of leachable uranium from solid samples such as mine tailings using scCO₂ containing organophosphinic acids such as Cyanex 301 and Cyanex 302 [49].

Chemistry of Complexes

Enokida *et al* studied the phase behaviors of the scCO₂-HNO₃-TBP system containing uranyl and lanthanide nitrates. They found that extraction of uranyl and lanthanide complexes occurs at different pressures and supported their findings using the modified Peng-Robinson equation of state with classical quadratic mixing rules [102]. Tomoika *et al* studied the kinetics of the dissolution of uranium oxides in the scCO₂-HNO₃-TBP system and showed that the reaction mechanisms for the dissolution of U₃O₈ and UO₂ are different [50]. Clifford *et al* modeled the extraction of uranium from HNO₃ matrix in a flow system containing TBP-scCO₂ using diffusion out of a sphere into a medium in which the extracted uranium is infinitely dilute [51]. Sawada *et al* used scCO₂ to determine the overall dissolution equation of the uranyl ion in HNO₃ with TBP and H₂O as $\text{UO}_2 + 4\text{HNO}_3 + 2\text{TBP} \rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} + 2\text{NO}_2 + 2\text{H}_2\text{O}$ [52]. A study of

laser-induced fluorescence by Addleman investigated the quenching mechanisms for the uranyl complex at different temperatures and pressures. It was found that bimolecular collisional dynamics associated with a gas phase as well as viscosity effects associated with the liquid phase are required to describe pressure quenching [53]. In order to predict extraction equilibria for uranyl nitrate and nitric acid between aqueous and tributyl phosphate-hydrocarbon diluent solutions, Yu *et al* derived activity coefficient equations for the $\text{HNO}_3\text{-UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ system [104].

Ultrasonication

The extraction of lanthanides, actinides and uranium into supercritical fluids using ultrasound was investigated by Wai *et al* and found to enhance extraction efficiency [54]. Samsonov *et al* used ultrasonication along with TBP, HNO_3 , thenoyltrifluoroacetylacetone (TTA) and scCO_2 to efficiently separate milligram amounts of uranium dioxide from plutonium, neptunium, and thorium [55]. Enokida *et al* report that the dissolution rate of uranium dioxide powders from glass beads using scCO_2 containing TBP, HNO_3 and H_2O with sonication was increased by an order of magnitude compared to experiments without sonication. [56].

Separation of Metals

Wai *et al* used TBP to selectively extract uranium from spent nuclear fuel containing cesium, strontium and technetium. They also used TTA but found the

extraction to be an order of magnitude lower than that of TBP [57]. Tofimov *et al* investigated the use of scCO_2 , TBP and HNO_3 in the separation of oxides of uranium from plutonium, neptunium, americium and europium oxides [58]. Smart *et al* developed a “dry” separation method for uranium and another metal in which the oxidation state of uranium is greater than (+4). The uranium and the other metal are dissolved in organic solvent then uranium is selectively extracted to scCO_2 . No HNO_3 is required for dissolution of the spent nuclear fuel [60]. A similar “dry” process developed by Samsonov *et al* used a CO_2 -phillic complexant to form a highly soluble $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complex, dissolving the UO_2 without water or organic solvent [59]. Uchiyama *et al* developed a new PUREX process to reduce TRU waste volume capable of separating neptunium and technetium from plutonium and uranium solutions [61]. Iso *et al* extracted uranium(VI) in HNO_3 and LiNO_3 into scCO_2 with TBP. Extraction of U(VI) increased with an increase in the concentration of TBP and a decrease in temperature, with an efficiency of >98%. Main fission elements such as cesium, strontium, barium, zirconium, molybdenum and palladium were hardly extracted into the scCO_2 [62].

Distribution Coefficient of Uranium

Meguro *et al* studied the distribution behavior of uranium in the TBP/ scCO_2 system and found that it was nearly independent of the concentration of uranium in the system. They also found that suppression of the extraction of the complex due to solubility limitations in the scCO_2 phase was unlikely [63]. Iso *et al* determined

distribution coefficients for extractions with TBP to scCO₂ for plutonium and uranium in HNO₃ [64]. Meguro *et al* formulated a linear relationship between the distribution ratio (D_U) of U(VI) and the density (ρ) of scCO₂: $\log D_U = a \log \rho + A + B$, where a is a proportional constant implying the solvation characteristic of the solute in scCO₂, A is a pressure-independent constant, and B is a variable determined by the distribution equilibrium of HNO₃. The equation was verified experimentally [65].

Chelating Agents and Modifiers

Kumar *et al* extracted uranium from tissue-paper matrix with scCO₂ containing methanol, TOPO and TBP. They found that scCO₂ with methanol alone extracted up to 76% of the uranium from the tissue matrix [66]. Shamsipur *et al* studied the solubility of uranyl nitrate in scCO₂ with methanol, which showed considerable solubility. Also studied in scCO₂ were co-extractants such as TBP, methylisobutyl ketone (MIBK), and acetylacetone (AA) from cellulose-based filter papers. The extraction efficiency followed the order TBP>MIBK>AA>MeOH. Eight potential chelating agents for uranyl ion extraction from filter paper to methanol-modified scCO₂ were bis(2-ethylhexyl)hydrogen phosphate (HDEPH), TOPO, DC18C6, dibenzoylmethane (DBM), 8-hydroxyquinoline (HOX), diphenylaminesulfonic acid (DPASA), 1,4-bis-[4-methyl-5-phenyl-2-oxazolyl]benzene (DMPOPOP) and TBP. TOPO and HDEPH showed the highest extraction efficiency [67]. Wai *et al* developed a method for the separation of metals from impurities using supercritical fluid extraction (SFE) based on solubility differences among the components. The following chelating agents, and mixtures

thereof, were used in combination with scCO_2 : β -diketones, phosphine oxides, phosphinic acids, carboxylic acids, phosphates, crown ethers, dithiocarbamates, phosphine sulfides, phosphorothioic acids, thiophosphinic acids and halogenated analogs of these agents [68]. Wai used fluorinated derivatives of hydroxamic acid for selective extraction of actinide metals from aqueous HNO_3 feed for the removal of contaminants from industrial waste [69]. Wai used TTA and TBP to extract uranyl ion from mine waste-water with 70% efficiency versus 38% without TBP [70]. Wai used methanol-modified scCO_2 containing a fluorinated β -diketone to extract U(VI) from sand and cellulose-based paper. Neat CO_2 consisting of TBP and one of the following fluorinated β -diketones was used to extract U(VI) from mine water and mine water-containing soil: hexafluoroacetylacetone (HFA), TTA, and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl octane-4,6-dione (FOD) [71].

Detection Methods

Addleman *et al* used on-line, time-resolved, laser-induced fluorescence for analysis of uranium extraction from HNO_3 solution with TBP-modified scCO_2 . They found extractions were first order in uranium, and the distribution coefficient of uranium increased with temperature and TBP concentration [72]. Further research from Addleman *et al* described the design of a spectroscopic flow cell for supercritical extraction. The use of standard or fiber optic spectrometers and two perpendicular paths adjustable in length allowed the cell to be used for absorption, emission, or scattering spectroscopy [73]. Sasaki *et al* determined concentrations of TBP-uranyl ion complex by

UV-vis spectrometry with a detection limit of 10^{-3} M. Molar absorptivity was seen to decrease with increasing density of scCO_2 [74]. Carrott and Wai designed a micro-scale; fiber optics-based system for the measurement of solubilities in scCO_2 for pressures in excess of 300 atm. The solubility of $\text{UO}_2(\text{TTA})_2$ was determined [75].

Solubility

Addleman *et al* used laser-induced fluorescence to measure solubilities of uranyl complexes with TTA, TBP, and TOPO [76]. Waller *et al* studied solubility of uranyl nitrate-TBP in scCO_2 by UV-vis spectroscopy. It was found have a solubility of 0.4291 M at 225 atm [77].

Others

Chiu *et al* used scCO_2 , TBP and TTA to sequentially separate uranium and PCBs in contaminated soil [87]. Meguro *et al* produced a review of the distribution coefficients of uranyl and plutonium complexes between aqueous and scCO_2 phases using TBP and diisodecyl phosphoric acid (DIDPA) in the extraction of spent nuclear fuels [88]. Murzin *et al* extracted uranium in the presence of butyl-3,3,4,4-tetrafluoro-2-methylbutyl-2-yl methylphosphonate up to 62-72% compared to only 35-45% with TBP. They extracted air-dried uranyl nitrate with scCO_2 containing TBP, TTA and water from the surface of stainless steel, rubber and asbestos to 75-97% [89].

1.4.3. Industrial Processing of Uranium

Uranium is mined in the form of pitchblende as U_3O_8 and, worldwide, is found as 0.006-0.011 wt % of the raw ore. As a brief overview of the industrial uranium purification process, the ore is crushed and leached in a solution of nitric and perchloric acid to ensure that the uranium is present in the (+6) oxidation state (as uranyl nitrate), at which it is more soluble. Extraction of uranium from the leachate involves solvent extraction in to a kerosene-type diluent/TBP phase as a uranium-TBP-nitrate complex. Small amounts of other metals (thorium, iron, molybdenum etc.) are extracted simultaneously. The extracted uranium is then recovered (or stripped) through a backwashing step and transforms back to the uranyl nitrate species [pc Dr. Bob Burk]. Secondary processes are used to increase selectivity for uranium for example, molybdenum is removed by carbonate stripping after the initial organic/TBP extraction, and iron is water-scrubbed. Post-extraction, solvent recovery is carried out through centrifugation, activated carbon, and other methods [19].

The organic solvent/TBP solution requires well-ventilated work areas, recovery equipment such as centrifuges, coalescers, activated-carbon treatment equipment among others, and produces large quantities of solvent-containing waste [19].

1.5. Uranium/Tributyl Phosphate/Supercritical Carbon Dioxide System

Uranium trioxide dissolved in nitric acid forms the uranyl nitrate salt which dissociates to UO_2^{2+} and NO_3^- (equation 1.5-1). A uranium complex forms in the

presence of TBP, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, and is extracted to scCO_2 with the following stoichiometry (equation 1.5-2).

1.5.1. Distribution of Species among Phases

As can be seen in Figure 1.5-1, the aqueous phase contains uranyl ion, nitrate ion, TBP, TBP complexed with uranyl ion as $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, and TBP complexed with nitric acid as HNO_3TBP , all according to their individual formation and distribution coefficients at cell equilibrium. The scCO_2 phase contains TBP, and complexes $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ and HNO_3TBP that have partitioned with concentrations determined by their formation and distribution coefficients.

Figure 1.5-1. Schematic diagram of species present in acidic aqueous and scCO_2 phases.

1.6. Selectivity of Extraction of Uranium to Supercritical Carbon Dioxide

Uranium is found in nature associated with other elements such as boron, chromium, iron, molybdenum, and thorium. In the uranium extraction industry, TBP is dissolved in Isopar-M (30 vol %), an industrial solvent consisting of saturated isoparafinics C-10 to C-13. This solution is used as the organic phase of a liquid-liquid extraction process designed to selectively extract uranium from the other metals present in the ore.

1.6.1. Theory of Selectivity

Selectivity is the ability of a solvent to preferentially extract one solute to the exclusion of other solutes co-dissolved in a solution. Through experimental design, the intermolecular interactions of solubility can be controlled permitting selective extraction. Selectivity is based on the principle of the Separation Factor β [18]

$$\beta = \frac{[A]_o/[B]_o}{[A]_w/[B]_w} = \frac{[A]_o/[A]_w}{[B]_o/[B]_w} = \frac{D_A}{D_B} \quad (1.6-1)$$

where A and B are individual solutes.

If one of the distribution coefficients is large and the other small, complete separation can be achieved. However, even if the separation factor is large but the smaller distribution coefficient is large enough that the two solutes are extracted

simultaneously, the undesired solute may require suppression or further separation may be required [18].

The separation factor may be applied specifically to metal chelates.

$$\beta = \frac{D_A}{D_B} = \frac{K_{f_A} \cdot K_{D_{x_A}}}{K_{f_B} \cdot K_{D_{x_B}}} \quad (1.6-2)$$

where K_f is the stability constant for the chelate in each phase and K_D is the relative solubility of the chelate in the organic phase. Equation (1.6-2) shows that the difference in stability constant, K_f affects the separation of the chelates as well as the relative solubilities of the chelates in the organic solvent [18].

Selectivity can be increased by modifying the oxidation state of the unwanted ions in solution and thereby preventing the formation of extractible complexes. It is also important to adjust the oxidation state of the ion of interest to maximize complex formation and extraction [18].

1.6.2. Importance of Selective Extraction of Uranium

The importance of selectivity in the uranium extraction process in the production of nuclear fuel is primarily based on the effect of the neutron cross-sections of other metals present in the ore with uranium. The cross-section is estimated from the radius of a nucleus and is measured in barns where $1 \text{ barn} = 10^{-24} \text{ cm}^2$. The radius is used to estimate the total reaction cross-section i.e. the sum of the probabilities per target nucleus for all nuclear reactions that take place for an incident particle-target combination [90].

Three neutrons are released from ^{235}U upon bombardment (equation 1.6-3). The presence of other elements in the uranium fuel can cause capture of the emitted neutrons based on their neutron capture cross-section and therefore these contaminating elements must be minimized.

Table 5 lists the natural abundance and neutron cross-sections of the elements included in “multi-element” experiments of this thesis [11].

Table 1.5-1. Major isotopes, % natural abundance, absorbance cross-section (for 2200 m/s thermal neutrons) of elements included in “multi-element” analyses [11].

Isotope	% Natural abundance	Absorbance cross section (barns)
^{10}B	19	3835
^{11}B	81	0.0055
^{52}Cr	83	0.76
^{53}Cr	10	18.1
^{50}Cr	4	15.8
^{54}Cr	3	0.36
^{56}Fe	92	2.59
^{57}Fe	2	2.48
^{54}Fe	6	2.25
^{92}Mo	15	0.019
^{94}Mo	9	0.015
^{95}Mo	16	13.1

Isotope	% Natural abundance	Absorbance cross section (barns)
^{98}Mo	17	0.127
^{97}Mo	10	2.5
^{98}Mo	25	0.127
^{100}Mo	10	0.4
^{232}Th	100	7.34
^{235}U	0.71	680
^{238}U	99.3	2.68

1.7. Statement of Purpose

The industrial processing of uranium produces large amounts of organic waste during the liquid-liquid separation stage of the extraction process. In addition to the environmental burden that the production and disposal of these solvents presents, an economic burden exists as well in the form of purchase and disposal costs. The use of supercritical carbon dioxide (scCO₂) in place of organic solvents in the extraction of uranium has been investigated by several research groups and has been proven to be viable. Extraction with scCO₂ has many advantages over organic solvents among which are high diffusivity and low viscosity leading to rapid mass transfer; upon gasification scCO₂ no longer retains its solvent properties hence desolubilization of the solute is simple; and CO₂ is readily available, recyclable, non-toxic and inexpensive.

Since preparation of the uranium ore for processing forms the uranyl ion (UO₂²⁺), a complexing agent or ligand is required to facilitate the movement of the UO₂²⁺ to the non-polar scCO₂ phase. Much research has been done on scCO₂ metal extraction systems using tributyl phosphate (TBP) as the complexing agent. This ligand is presently used in the uranium industry to distribute UO₂²⁺ from the aqueous phase to the organic phase in the separation stage of processing. However, the fundamental mechanism of UO₂-TBP-CO₂ complex formation and distribution is not well understood.

One goal of this project therefore was to fill this gap in the knowledge of the UO₂-TBP-CO₂ extraction system by studying the system at equilibrium to determine where the uranium complex forms and from which phases the components of the complex are drawn. A second goal was to determine the selectivity of the TBP/scCO₂ extraction

procedure for uranium in the presence of boron, iron, molybdenum, thorium and chromium, elements commonly associated with uranium in the ore and which need to be removed during the purification process.

2. Equipment and Methods

2.1 Equipment

2.1.1. Description of Supercritical Fluid Extraction Apparatus

All experiments involving supercritical carbon dioxide (scCO_2) were carried out using a Suprex SFE/50 Supercritical Fluid Extractor instrument, a photograph of which appears in Figure 2.1-1 and plumbing diagram in Figure 2.1-2. A Suprex syringe pump (236 mL capacity) was used to produce supercritical carbon dioxide from commercial grade liquid carbon dioxide (Praxair, Mississauga, Ontario). As required, one of two stainless steel high-pressure cells of volume 100 mL (Figure 2.1-3) or 1 mL (Figure 2.1-4) was plumbed into the system between the syringe pump and the collection vessel using two SSI two-way high-pressure shut-off valves to allow isolation of the cell while the system reached equilibrium.

The 100 mL vessel was designed and constructed by the Carleton University Science Technology Centre and has the following specifications (see Appendix II). Body: AISI 316 (American Iron and Steel Institute: chromium-nickel with 2-3% molybdenum, 16-18% chromium) stainless steel; cap: hardenable stainless steel hardened to Rockwell C 50. The inside surface of the cap was machined such that a Teflon seal could be inserted. Fittings and tubing (0.030" ID X 1/16"OD), were of AISI 316 stainless steel. A K-type high-temperature flexible wire probe (0.063", Cole Parmer, Vernon Hills, IL) was swaged into the side of the cell with 1/16" nut and ferrules

Figure 2.1-1. Supercritical fluid extraction instrument. 1. Syringe pump. 2. Controller. 3. oven. 4. thermocouple and microprocessor. 5. collection vessel.

Figure 2.1-2. Schematic diagram of high-pressure supercritical fluid extraction system.

Figure 2.1-3. 100 mL stainless steel high-pressure reaction cell.

Figure 2.1-4. 1 mL high-pressure stainless steel reaction cell.

(Swagelok, Solon, OH) and connected to an Omega microprocessor thermometer (model HH22) for constant monitoring of cell conditions. PEEK (polyetheretherketone) tubing (0.50 mm ID X 1/16" OD, 4500 psi, Upchurch Scientific, Oak Harbor, WA), was connected to stainless steel tubing by a PEEK union (PEEK ZDV union, 0.020" hole, Upchurch Scientific) when required.

The 1 mL high-pressure stainless steel vessel was purchased from Suprex Corporation (no longer in existence) and neither engineering diagram nor steel composition are available.

2.1.2. Sampling Apparatus for Determination of Solubility of Dibenzo-24-crown-8 in Supercritical Carbon Dioxide

The Suprex SFE/50 was fitted with a 6-port high-pressure valve (Figure 2.1-5) plumbed as follows:

port 1: 0.030" stainless steel tubing with SSI two-way shut-off valve (Supelco,

Bellefonte, PA) leading to collection vessel

port 2: 0.030" ID stainless steel tubing with SSI two-way shut-off valve and Luer Lock

fitting to admit methanol for rinsing out sample loop

ports 3 and 6: connected by stainless steel sample loop of volume 0.122 mL

port 4: 0.030" stainless steel tubing for admission of supercritical carbon dioxide to cell

port 5: plugged.

Figure 2.1-5. Schematic diagram of apparatus for solubility of DB24C8 in scCO₂ experiments

A stainless steel, high-pressure flow-through sample cell of 1 mL volume (Figure 2.1-4), was plumbed in-line between the syringe pump and the 6-port high-pressure valve. Both the sampling cell and the valve were located in the Suprex oven.

2.1.3. Sampling Apparatus for Solubility of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

For the determination of the solubility of 1,4,10,13-tetraoxo-7,16-diazacyclooctadecane (2N) in hexane, a home-made high-pressure system consisting of the following components was assembled using stainless steel tubing (0.030" ID, 1/16" OD): Bio-Rad 1330 pump, Waters Differential Refractometer R401, pressure gauge (Span Instruments, Plano, Texas) Rheodyne Injector (Supelco) with 120 μ L sample loop (Figure 2.1-6). A NESLAB RTE-8 Refrigeration Unit provided a constant temperature water bath. Varian Star Workstation 2002 was used for peak integration.

2.1.4. Sampling Apparatus for Solubility of Tributyl Phosphate

A 100 mL stainless steel high-pressure cell containing tributyl phosphate (TBP) and a stir bar was charged with CO₂ from the syringe pump via stainless steel tubing (0.030" ID, 1/16" OD) to an inlet (1/16" Swagelok to 1/4" universal pipe thread fitting) in the cap. Three SSI valves were plumbed into the system as follows: into the inlet tubing

Figure 2.1-6. Schematic diagram of apparatus for solubility of 1,4,10,13-tetraoxo-7,16-diazacyclooctadecane (2N) in hexane experiments.

and outlet tubing to allow the cell to be isolated during equilibration; a three-way shut-off directly upstream of the cell to allow evacuation of the cell contents to the fume hood. Samples of the scCO₂ phase were collected through a silica restrictor (15 µm ID), the length of which was varied in order to adjust the flow rate of scCO₂ from the cell, with the tip inserted into a glass delivery tube wrapped in heating tape (Figure 2.1-7) to prevent solidification of the CO₂ as it cooled upon expansion. The mouth of the collection vessel was closed with a two-hole rubber stopper allowing the restrictor to pass into the collection vessel through one hole. The second hole accommodated stainless steel tubing connected to Tygon tubing which was in turn connected to a 10 mL bubble-type flow meter in order to measure the volume of carbon dioxide leaving the cell. The cell was located in the Suprex oven atop a stir plate which was controlled externally with a 10 A Powerstat Variac. Several variations of the collection vessel were employed to trap the TBP for gravimetric analysis:

1. glass U-tube ¼" and ½" ID
2. U-tube submerged in ethanol bath
3. U-tube containing glass wool submerged in ethanol bath
4. U-tube containing glass wool and activated charcoal submerged in ethanol bath

2.1.5. Sampling Apparatus for Uranium Extraction Experiments

Apparatus was similar to that of section 2.1.4. (Figure 2.1-8) was used to sample uranium with the exception that the aqueous phase (port 2) was sampled through stainless steel tubing which was fitted with a PEEK union and PEEK tubing (0.050 mm ID X

Figure 2.1-7. Schematic diagram of apparatus for solubility of TBP in scCO₂ experiments.

Figure 2.1-8. Schematic diagram of sampling apparatus for determination of concentration of TBP, HNO_3^- , H^+ and uranium in HNO_3 - scCO_2 experiments. 1: scCO_2 phase sampling port, 2: aqueous phase sampling port.

1/16" OD). The two-way SSI shutoff valve was replaced with a PEEK high-pressure micro-splitter valve (P460S, Upchurch Scientific) with graduated flow. A 10 cm length of PEEK tubing served as the restrictor to deliver the sample to the collection vessel.

2.1.6. Sampling Apparatus for Nitrate Experiments

Apparatus similar to that of section 2.1.4. (Figure 2.1-8) was used to sample the scCO₂ phase (Figure 2.1-8, port 2) with the exception that the 10 mL bubble-type flow meter was replaced with a 400 mL meter of similar design.

2.2. Methods

2.2.1. Thermodynamic Properties of Complexing Agents

2.2.1.1. Solubility of 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane in Water

A mass of white, crystalline powder 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2N) (97%, Aldrich) was added to a known volume of distilled water, with stirring, until a quantity of the solid remained undissolved on the bottom of the flask (>30 h). The vial was then suspended in 40°C water and more 2N was added, again until solid remained on the bottom of the flask.

2.2.1.2. Solubility of 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane in Hexane

To a known volume of hexane (Fisher, Optima grade), was added 0.4 g 2N with stirring (>24 h), until crystals remained on the bottom of the vial. The vial was then suspended in water at 40°C and 2N was added until crystals once again remained at the bottom of the vessel. Samples (taken at 30 min intervals to ensure that the system had reached equilibrium) were withdrawn, diluted with hexane, and analyzed by a home-made high-pressure system (Figure. 2.1-6) with 100% hexane mobile phase, flow rate 1.5 mL/min. Since derivatization of the sample was not possible, analysis was carried out by refractive index detection.

2.2.1.3. Solubility of Dibenzo-24-crown-8 in Supercritical Carbon Dioxide

A mass of dibenzo-24-crown-8 (DB24C8) (98%, Aldrich) was placed in a vacuum dryer and allowed to reach constant mass. The dry, white powder, was mixed with previously washed and dried glass beads (untreated 45/60 mesh, Chromatographic Specialties) to a volume of 1 mL and was placed into a 1 mL high- pressure stainless steel cell (Figure. 2.1-4). The cell was placed into the Suprex oven at an appropriate temperature and was connected in-line via stainless steel tubing (0.030"ID X 1/16"OD) between the syringe pump and a 6-port high-pressure valve (Figure 2.1-5). After the admission of supercritical carbon dioxide (scCO₂) to the cell at an appropriate pressure, the contents were given sufficient time to reach equilibrium (> 30 min). Samples were collected into methanol by first placing the 6-port valve into the load position, which allowed the sample loop to be filled with DB24C8-scCO₂ solution, followed by the inject position, which allowed the sample to proceed to the collection vessel. While still in the inject position, methanol (via a syringe with Luer Lock fitting) was forced through the loop, valve and tubing into the collection vessel to ensure that the entire sample had been flushed from the collection system. Samples were analyzed in methanol with a Varian Cary 3 UV Visible Spectrophotometer at 276 nm using methanol as a reference.

2.2.1.4. Solubility of Tributyl Phosphate in Supercritical Carbon Dioxide

A volume of tributyl phosphate (TBP), 35 mL, and a stir bar were placed into a 100 mL stainless steel high-pressure cell (Figure. 2.1-3). The cell was sealed and placed

into the Suprex oven at an appropriate temperature (Figure. 2.1-7). scCO_2 was admitted to the cell via a two-way shut-off valve and the cell was stirred for > 8 hours. The stirrer was then turned off and phases were allowed to equilibrate for > 20 minutes. A second two-way shut-off valve located in the outlet tubing was opened allowing scCO_2 and dissolved TBP to flow into the silica restrictor which passed through one hole of a two-hole stopper. The volume of CO_2 sampled was measured via stainless steel tubing that passed through the second hole in the stopper and led to a 10 mL bubble-type flow meter. The flow was regulated by varying the length of the restrictor. In order to trap the TBP quantitatively, the end of the restrictor was attached to a hand-crafted glass U-shaped tube. Collection was attempted as follows: with the tube submerged in a low temperature ethanol bath; with glass wool inserted into the tube; with activated charcoal in the tube; and various combinations of the above. The glass U-tube was weighed prior to the collection of TBP and again after sampling to determine the mass of TBP collected.

2.2.2. Extraction of Uranium with Crown Ethers, Calixarene, and Synergists

Into a 14 mL vial were placed 1 mL of an appropriate concentration of uranium trioxide dissolved in 2.73 M HNO_3 (see Table 3.3-1), 1 mL of an appropriate concentration of crown ethers or calixarene (see below) dissolved in organic solvent, an appropriate mass of synergist, and 9 mL of organic solvent.

- 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2N)
- dibenzo-24-crown-8 (DB24C8)

- dicyclohexano-24-crown-8 (DC24C8)
- dicyclohexano-18-crown-6 (DC18C6)
- 18-crown-6 (18C6)
- calyx[6]arene (1mL 13 000 ppm, 1 mL 60 000 pm U, 9 mL CHCl₃)
- the above compounds combined with synergist
 - perfluoro-1-octanesulfonic acid, tetraethylammonium salt (PFOSA)

The mixture was shaken for 30 min on a wrist-action shaker. The phases were allowed to separate for 30 min and were then pipetted into a separatory funnel. Each phase was removed to a porcelain crucible and evaporated to dryness. The contents were ashed in a muffle furnace at 200°C for one hour and at 500°C for 8 hours to mineralize the crown and synergist compounds. One mL of concentrated nitric acid was added to each crucible to dissolve the uranium residue followed by rinsing with 9 mL of distilled water. Dilution of the samples was carried out as required for analysis by inductively coupled plasma emission spectroscopy (ICP-ES) under the following conditions. The linear dynamic range was determined to be 0-730 ppm for uranium.

Spectrometer: Thermo Instruments IRIS CID ICP-ES Spectrometer

Wavelength: 263.5 nm

RF power: 1150 watts

Plasma flow: 15 L/min

Aux. flow: 1.0 L/min

Nebulizer flow: 1.0 L/min (32.06 psi, cross-flow nebulizer)

Solution uptake rate: 1.0 mL/min

Signal Integration Time: 10 sec (4 replicates)

Typical measurement precision at 50ppm: < 1-2% RSD

The calix[6]arene-uranium samples were analyzed by mass spectrometry at the University of Ottawa Mass Spectrometry Centre by Clem Kazakoff under the following conditions:

Micromass Quattro LC triple quadrupole mass spectrometer

Needle voltage: 3.8-4.2 V

Solvent: 1:1 CH₃CN : MeOH

2.2.3. Extraction of Uranium with Tributyl Phosphate

2.2.3.1. Sampling of Aqueous Phase for Tributyl Phosphate at Atmospheric Pressure

In order to study the distribution of the TBP-uranyl ion-nitrate complex, UO₂(NO₃)₂·2TBP, in the scCO₂-HNO₃ system, the concentration of the TBP ligand must be known in both phases.

To determine the concentration of TBP in the aqueous phase prior to pressurization, 4.1 mL TBP (in excess of the solubility) was combined with

1. 50 mL 2.73 M HNO₃
2. 50 mL 2.73 M HNO₃, 5.24 x 10⁻⁴ moles uranium

3. 50 mL 2.73 M HNO₃, 1.05 x 10⁻³ moles uranium

In order to hasten the establishment of equilibrium, each solution was stirred for 30 h and the TBP and aqueous phases were left to separate for 48 h. A micro-syringe was used to withdraw 1.0 mL of the aqueous phase from below the surface (undissolved TBP formed a layer above the aqueous phase) which was then extracted with 3 × 3 mL 2.73 M HNO₃-saturated DCM in a 30 mL separatory funnel. The organic phase was collected and the concentration of TBP was determined by GC-FID under the following conditions.

Column Specifications:

DB-5 (J & W Scientific, Folsom, CA)

ID: 0.25 mm

Film thickness: 0.25 Å

Length: 30 m

GC-FID Temperature program:

Initial column temperature: 80°C

Hold: 2 min

Final temperature: 200°C

Ramp: 10°/min

Hold: 0 min

Injector temperature: 280°C

Detector: 280°C

To determine the liquid-liquid extraction recovery of TBP, an appropriate volume of TBP was added to 25 mL 2.73 M HNO_3 and the contents were stirred for 22 hours. The TBP was extracted to HNO_3 -saturated DCM and analyzed by GC-FID.

2.2.3.2. Sampling of Aqueous Phase for Tributyl Phosphate at High Pressure

Into a 100 mL high-pressure cell were placed 50 mL 2.73 M HNO_3 , an appropriate mass of uranium trioxide (2×10^{-3} M uranium), an appropriate volume of TBP (0.15 moles) and a stir bar. Under cell conditions of 40–70°C and 80 to 300 atm, aqueous phase samples were withdrawn from the cell via port no. 2, Figure 2.1-8 after the contents of the cell had been stirred for 5 min to equilibrate, with an additional five minute phase separation period. Using a micro-splitter valve, samples of approximately 1 g were collected into previously weighed 6.5 mL vials. The vials were reweighed, and the contents were extracted to HNO_3 -saturated DCM in 30 mL separatory funnels. GC-FID was used to quantify the concentration of TBP.

2.2.3.3. Sampling of Aqueous Phase for Hydrogen Ion and Nitrate at Atmospheric Pressure

Since TBP is known to form complexes with nitric acid as HNO_3TBP , as well as the uranyl ion, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, in order to understand the $\text{UO}_2\text{-TBP-NO}_3$ system, it is necessary to know the concentration of NO_3^- in the aqueous and scCO_2 phases. The concentrations of NO_3^- and H^+ were taken to be equal since the only source of NO_3^- is

nitric acid, a strong acid with $K_a = 28$, and therefore the concentration of NO_3^- was found by determining the concentration of H^+ . To determine the concentration of H^+ , the following experiments were carried out and the aqueous solutions were titrated with NaOH standard (with phenolphthalein as the indicator). Each solution was stirred for 30 min.

- 50 mL 2.73 M HNO_3 , 1.33×10^{-4} moles U

- 50 mL 2.73 M HNO_3 , 1.33×10^{-4} moles U, 0.015 moles TBP

2.2.3.4. Sampling of Aqueous Phase for Nitrate at High Pressure

In a 100 mL stainless steel high-pressure cell were placed 50 mL of distilled water or 2.73 M HNO_3 and an appropriate amount of TBP and uranium trioxide. The following aqueous phases were extracted with scCO_2 .

1. H_2O (50 mL)
2. HNO_3 (50 mL)
3. HNO_3/TBP (50 mL, 0.015 moles TBP)
4. $\text{HNO}_3/\text{TBP}/\text{U}$ (50 mL, 0.015 moles TBP, 10^{-3} U)

In order to measure the concentration of nitrate at temperatures of 40 -70°C and pressures of 80-300 atm, the scCO_2 phase was sampled through port no. 1 in Figure 2.1-8. The micro-splitter valve was adjusted to approximately 20 – 30 mL/min flow of CO_2 . The CO_2 flowed through the restrictor (which passed through one of two airtight holes in a rubber stopper) into a previously weighed 6.5 mL vial containing ~5

mL of distilled water. Through the second hole passed stainless steel tubing leading from the collection vessel to a 400 mL bubble-type flow meter. A volume of 387 mL of carbon dioxide flowed through water in the collection vessel, depositing dissolved nitrate. The nitrogen concentration was determined by ion chromatography (Paracel Laboratories Ltd., Ottawa, ON).

2.2.3.5. Sampling of Aqueous Phase for Hydrogen Ion and Uranium at High Pressure

Into a 100 mL high-pressure cell were placed 2×10^{-3} M uranium in 50 mL 2.73 M HNO_3 and 0.015 moles of TBP. At cell conditions of 40-70°C and 80-300 atm, after five minutes of equilibration time, with stirring, and a five minute phase separation period, aqueous phase samples were withdrawn from the high-pressure cell through port no. 2 in Figure 2.1-8. Using the micro-splitter valve, aqueous phase samples of approximately 1 g were collected into previously weighed 6.5 mL vials. The vials were reweighed, and hydrogen ion samples were titrated with NaOH standard (with phenolphthalein as the indicator).

Uranium samples were sent for analysis by ICP-MS.

3. Results and Discussion

3.1. Thermodynamic Properties of Complexing Agents

3.1.1. 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane (2N)

Experiments to determine the solubility of 2N in water and hexane were carried out because hexane has similar solvation properties to those of supercritical carbon dioxide [26] [25] and it was hypothesized that 2N would be a suitable complexing agent for the extraction of uranium from water to scCO_2 .

3.1.1.1. Solubility of 2N in Water

After continually adding 2N to 5 mL of water at 40°C the solution became thick and viscous. It was observed that additional 2N was unable to dissolve due to the fact that the solution had become too dry. Based on this, the solubility of 2N in water at 40°C is at least 0.0567 mole fraction.

3.1.1.2. Solubility of 2N in Hexane

The solubility of 2N in hexane (Figure 3.1-1, Table 3.1-1) was determined at six temperatures and the solubility was found to increase with increasing temperature.

Figure 3.1-1. Solubility of 2N in hexane versus temperature at 26-36°C.

Table 3.1-1. Solubility of 2N in hexane at 26-36°C.

Temperature (°C)	Solubility (ppm)	Standard deviation
26.2	900	200
30.4	1800	300
32.4	2400	500
33.0	2200	200
34.0	3500	200
35.5	2600	500

It was not possible to accurately predict a partition coefficient for 2N between hexane and water based on its solubilities in these two pure solvents due to the impossibility of precisely defining a solubility of 2N in water, but the partition coefficient is likely less than 940 based on the known solubility in hexane, and the minimum solubility in water.

3.1.1.3. Enthalpy of Solution of 2N

The enthalpy of solution of 2N in hexane, using the slope of the curve of the log solubility versus $1/T$ ($T = 299\text{--}309\text{ K}$) in Figure 3.1-2, was found to be $41 \pm 5\text{ kJ mol}^{-1}$ and the entropy of solution was $160 \pm 20\text{ J mol}^{-1}\text{K}^{-1}$. ΔH was positive indicating that the

Figure 3.1-2. Log solubility of 2N in hexane versus $1/T$ for 299-309 K. (Uncertainty is $\pm 12\%$.)

solubility reaction required more energy to break the crystalline structure of solid 2N than was given off by the formation of 2N-hexane bonds. Also, because 2N is moving from the solid state (an ordered state) to dissolution in hexane (a less ordered state), it was expected that ΔS would be positive.

3.1.2. Solubility of Dibenzo-24-crown-8 (DB24C8) in Supercritical Carbon Dioxide

The solubility of DB24C8 in scCO_2 was determined at two densities at 40°C. The results can be seen in Table 3.1-2 and Figures 3.1-3, 3.1-4. These experiments were done as an introduction to supercritical fluid work. The results, when compared to literature values [91], provided an indication of the accuracy that can be achieved when sampling the scCO_2 phase.

Table 3.1-2. The solubility of DB24C8 in scCO_2 at 40° C.

Pressure (atm)	Density (g mL^{-1})	Experimental solubility (mole fraction)	Experimental solubility (g L^{-1})	Literature solubility (mole fraction) [91]
200	0.847	$(18 \pm 2) \times 10^{-6}$ n = 5	0.15 ± 0.02 n = 5	$(21.8 \pm 0.4) \times 10^{-6}$ n = 3
240	0.881	$(23 \pm 4) \times 10^{-6}$ n = 12	0.21 ± 0.03 n = 12	$(31.2 \pm 0.6) \times 10^{-6}$ n = 3

Figure 3.1-3. Mole fraction of DB24C8 in scCO₂ versus temperature at 200 atm showing experimental values and literature values (uncertainty $\pm 2\%$) [91].

Figure 3.1-4. Mole fraction of DB24C8 in scCO₂ versus temperature at 240 atm showing experimental values and literature values (uncertainty $\pm 2\%$) [91].

Although the experimental values are an average of 28% lower than the literature values, the trend in lower solubility at lower density seen in the experimental data agrees with the literature.

Shamispur's data [91] (Figures 3.1-3, 3.1-4) show that at constant temperature DB24C8 is more soluble at higher scCO₂ density. This can be explained by the fact that there is a greater number of CO₂ molecules available to solvate the DB24C8 molecules at higher density (or higher pressure). However, both Figures 3.1-3, 3.1-4 indicate that as the temperature increases (and the density decreases) the solubility actually increases. (One would expect the solubility to decrease as the density decreases.) Shamispur found that a change in behaviour takes place in the region of 160 atm. Above this pressure, solubilities increase both with increasing temperature and pressure but below 160 atm, solubilities increase with increasing pressure but decrease with increasing temperature. Shamispur attributes this change in behaviour to the effect of temperature on vapour pressure, density and molecular interactions of the supercritical fluid [91]. Darr and Poliakoff [25] state that a decrease in solubility is expected as a supercritical fluid is heated at constant pressure due to a decrease in density, but that further heating causes increased solubility because the vapour pressure of the solute rises proportionately faster than the density of the fluid falls.

3.1.3. Tributyl Phosphate

3.1.3.1. Solubility of Tributyl Phosphate in Supercritical Carbon Dioxide

Tributyl phosphate (TBP) was chosen as a ligand to carry the uranyl ion from the acidic aqueous phase to the scCO₂ phase in this research. In order to determine an appropriate concentration of TBP to add to the cell, it was necessary to determine the solubility of TBP in both the aqueous and scCO₂ phases to ensure that there would not be excess, i.e. undissolved, TBP present in the cell under experimental conditions.

The solubility of TBP in the scCO₂ phase was measured at 60°C and 148 atm by sampling the CO₂ phase. This measurement proved to be challenging and many different methods of trapping the gaseous TBP were tried. Initially, the restrictor leaving the cell was connected through a two-hole rubber stopper to a pre-weighed collection vessel containing glass wool. The second hole allowed the expanded CO₂ to leave the vessel via tubing (after having deposited the dissolved TBP on the glass wool) and to continue to a flow meter so that the flow, and thus the volume, of CO₂ sampled could be measured. Because escaping gaseous TBP was detected (TBP has a penetrating odour so it was immediately obvious when even small amounts had escaped from the collection vessel) the collection vessel was replaced with a hand-crafted, pre-weighed, U-shaped glass tube containing glass wool. Gaseous TBP escaped again so activated carbon was added to the U-tube, but the TBP was still not captured. At this point, the U-tube was immersed in an ethanol bath to lower the vapour pressure of the TBP during collection. Unfortunately, the TBP froze and the flow of CO₂ was impeded. Problems were also encountered when trying to weigh the U-tube. It was not possible to attain a constant weight since, as the tube warmed, TBP began to escape and also because CO₂ that had adsorbed onto the charcoal desorbed as tube warmed up.

It is thought that some of the difficulty encountered in collecting the gaseous TBP may also have been due to the valve used to regulate the flow of the CO₂-TBP solution from the cell. This valve was not designed to deliver metered flow and therefore the sample leaving the cell was composed of both gaseous and liquid TBP causing the flow to pulse and be difficult to regulate.

Figure 3.1-5 shows the solubility obtained by eight different methods used to trap TBP during solubility experiments, as well as the literature value [92]. The fact that most of the measured values fall below the literature value of 1.1 M indicates that TBP was indeed escaping before being collected. It is highly unlikely that these lower values represent a lack of equilibrium in the cell because a flow rate of 4–10 µL/min would not disturb the equilibrium. Based on these results, it was decided to sample the aqueous phase in subsequent experiments.

3.1.3.2. Thermodynamics of TBP Partitioning under Uranium Extraction Conditions

The partitioning of TBP between the aqueous and scCO₂ phases during the extraction of uranium is an important phenomenon. To understand the extent of extraction of uranium, it must be understood how the concentration of TBP in each phase varies with system variables such as pressure, temperature and composition of each phase in terms of the other components, CO₂, water and nitric acid.

Measurements of the partitioning of TBP between the two phases are presented here. In order to understand the partitioning of TBP, its solubility in scCO₂ and in aqueous nitric acid were measured. An estimate of a partition coefficient is simply the

Figure 3.1-5. The apparent solubility of TBP in scCO₂ at 60°C and 148 atm with various flow rates of scCO₂ through the 100 mL cell.

ratio of solubilities in the two pure solvents. Any deviation of the partition coefficient from this ratio gives an indication of the non-ideality of the system and is due to dissolution of water in the scCO₂ phase, CO₂ in the aqueous phase, and formation of complex species such as HNO₃TBP and UO₂(NO₃)₂ · 2TBP. After determining [TBP]_(aq) and using the result to calculate the [TBP]_(CO₂), it was possible to determine the value of the partition coefficient, K_{TBP}. From the slopes of the curves of the plots of ln K versus 1/T (T = 313-343 K), ΔH_{solution} and ΔS_{solution} for TBP in the scCO₂-2.73 M HNO₃ system were determined at five different densities of scCO₂ (see Table 3.1-3).

Table 3.1-3. Experimental values of ΔH_{solution} and ΔS_{solution} obtained from the equilibrium concentrations of TBP in acidified water and scCO₂; and ΔH and ΔS values derived from the ratio of the solubility of TBP in scCO₂ [92] and water [113] at various densities of scCO₂.

density scCO ₂ (g mL ⁻¹)	ΔH partitioning experimental (kJ mol ⁻¹)	ΔS partitioning experimental (J mol ⁻¹ K ⁻¹)	ΔH from solubilities of TBP in scCO ₂ and H ₂ O (kJ mol ⁻¹) [113,92]	ΔS from solubilities of TBP in scCO ₂ and H ₂ O, (J mol ⁻¹ K ⁻¹) [113,92]
0.3	-39.6	-67.6		
0.4	-39.9	-68.7	8.0	79.4
0.5	-37.3	-60.5	13.3	98.3
0.6	-31.9	-43.5	16.9	110
0.7	-24.2	-19.5	14.3	103

$\Delta H_{\text{experimental}}$ was found to be negative over all densities of scCO₂ sampled. As the density increased, the value of ΔH increased (i.e. became more positive) as can be seen in Figure 3.1-6. A negative value for ΔH indicates that more energy was given off during the formation of TBP-CO₂ bonds than was absorbed to break TBP-H₂O bonds at equilibrium. However, as the density increased, ΔH was seen to increase indicating that density-dependent changes were taking place in the cell which were influencing the partitioning of TBP from the aqueous phase to the CO₂ phase. It was expected that ΔH would become more negative with increasing density of CO₂, because, at higher densities, scCO₂ is typically a stronger solvent.

$\Delta S_{\text{experimental}}$ was found to be negative over all densities sampled (Figure 3.1-7). ΔS increased as the density of scCO₂ increased from 0.4-0.7 g mL⁻¹ indicating that the TBP-solvent system became less ordered as the TBP moved from the aqueous to the scCO₂ phase. This was unexpected and suggests that TBP may be present in a more ordered state, perhaps complexed with nitric acid.

Variation of the experimental values of ΔH and ΔS from those derived from the ratio of the solubilities of TBP in scCO₂ and water indicate that the experimental system is non-ideal. Figures 3.1-6, 3.1-7 and Table 3.1-3 show calculated values (i.e. theoretical values) of ΔH and ΔS derived from the plot of $\ln K$ (from the ratio of TBP solubilities in scCO₂ and water) versus $1/T$ for 313-343°C at different densities. These theoretical values for ΔH indicate that, based on two isolated phases, the partitioning of TBP from the aqueous to scCO₂ phase would be an endothermic reaction with $\Delta H > 0$. At constant density, a comparison of $\Delta H_{\text{experimental}}$ and ΔH_{ideal} indicates that there are factors present under experimental conditions that are making the system non-ideal. The increase in

Figure 3.1-6. Experimental $\Delta H_{\text{solution}}$ for TBP in scCO_2 versus density scCO_2 for 40-70°C compared to ideal data derived from the solubility of TBP in scCO_2 [92] and water data [113].

Figure 3.1-7. Experimental $\Delta S_{\text{solution}}$ for TBP in scCO_2 versus density scCO_2 for 40-70°C compared to ideal data derived from the solubility of TBP in scCO_2 [92] and water data [113].

$\Delta H_{\text{experimental}}$ as the density increases could be the result of several different interactions or combinations thereof.

First, it is possible that there are interactions in the aqueous phase that are interfering with the partitioning of TBP from the aqueous phase to the CO₂ phase (i.e. increasing the energy required to break the bonds in the aqueous phase). This may be explained by the fact that as the density of scCO₂ increases, according to Henry's Law, more CO₂ dissolves in the aqueous phase [40] (Figure 3.1-8). Due to the low pH of 2.73 M HNO₃ (-0.436) this CO₂ will be in the form of undissociated carbonic acid according to the following equilibrium equations (3.1-1, 3.1-2), with the equilibrium in equation (3.1-2) lying far to the left.

Since the observed increase in ΔH coincides with an increase in [H₂CO₃] in the aqueous phase as the density increases, the interactions between carbonic acid and TBP may be influencing the solubility of TBP in the aqueous phase (making it more soluble) and thus may be responsible for this increase in ΔH .

A second possibility is that partitioning of water to the scCO₂ phase may be responsible for the dissolution of nitric acid as an ion pair in the scCO₂ phase resulting in suppression of the partitioning of the TBP. According to Jackson *et al* [93], water added to scCO₂ can greatly influence the solubility of polar species.

Figure 3.1-8. Mole fraction of CO₂ in water under supercritical conditions (based on mL CO₂ per g water) [113].

A third possibility is that since TBP is much less soluble in water than in scCO_2 , the presence of water in the CO_2 would be expected to lower the solubility of TBP in the CO_2 phase below that in pure scCO_2 .

Fourth, the presence of nitric acid in the system and thus the formation of the HNO_3 -TBP and $\text{UO}_2\text{-NO}_3$ -TBP complexes, may have an effect on the partitioning of the TBP under experimental conditions.

And finally, another source of non-ideality could be that the solubility of TBP in water may not accurately reflect the solubility of TBP in 2.73 M HNO_3 .

3.2. Thermodynamics of Uranium Partitioning

3.2.1. Enthalpy and Entropy of Partitioning in Supercritical Carbon Dioxide

ΔH and ΔS for the partitioning of uranium in the scCO_2 - 2.73 M HNO_3 system were determined at three different densities of scCO_2 from the slopes of the curves of the plots of $\ln D_U$ versus $1/T$ ($T = 313\text{-}343$ K) (see Table 3.2-1). ΔH was found to be negative and, as the density of the scCO_2 increased, ΔH became more negative. Therefore, as the density increased, more energy was released by the formation of bonds between CO_2 molecules and the uranyl complex than was consumed in breaking bonds between the uranyl ion and water molecules plus any other species in the aqueous phase. ΔS was also found to be negative and, as the density increased, it became more negative. This indicates that at higher density the uranyl complex is in a more ordered state in the scCO_2 phase than is the uranyl ion in the aqueous phase.

Table 3.2-1. ΔH and ΔS experimental values for the partitioning of uranium from 2.73 M HNO_3 to scCO_2 .

Density scCO_2 (g mL^{-1})	ΔH experimental (kJ mol^{-1})	ΔS experimental ($\text{J mol}^{-1} \text{K}^{-1}$)
0.6	-12.5	-32.3
0.7	-26.0	-73.3
0.8	-47.0	-139

3.3. Extraction of Uranium Complexes with Crown Ethers, Calixarenes and Synergists

3.3.1. Liquid-liquid Extraction of Uranium

3.3.1.1. 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane (2N) (Carbon, Oxygen and Nitrogen Atoms in Ring)

The extraction of uranium from an acidified aqueous phase into chloroform, dichloromethane, toluene and hexane was attempted using 2N as the complexing agent. Synergist perfluoro-1-octanesulfonic acid, tetraethylammonium salt (PFOSA) was added to the aqueous phase to enhance the transfer of uranium. Unfortunately, no measurable amounts of uranium were extracted due to, it is thought, the protonation of the amine groups in the ring at the low pH required to prevent hydrolysis of the uranyl ion. (A positive charge on the ring would prevent complexation with the positively charged

uranyl ion, UO_2^{2+} and possibly prevent any complex from partitioning into an organic solvent [94].

3.3.1.2. Crown Ethers (Carbon and Oxygen Atoms in Ring) and Synergists

Uranium complexed with 18-crown-6 (18C6), dicyclohexano-18-crown-6 (DC18C6), dicyclohexano-24-crown-8 (DC24C8) and dibenzo-24-crown-8 (DB24C8) was extracted to chloroform and hexane in the presence of, and without, synergist PFOSA. It can be seen in Table 3.3-1 that although the extraction efficiencies were low, uranium mass balances were acceptable. It can be noted that in several experiments the addition of PFOSA actually reduced D_U .

Table 3.3-1. Distribution coefficients of uranium (D_U) for 2.73 M HNO_3 and organic solvents with various crown ether/perfluorinated counter ion combinations.

crown / solvent	moles of crown	moles of uranium	synergist	moles of synergist	D_U Average	mass balance
DB24C8 in CHCl_3	3.03×10^{-5}	2.52×10^{-4}			$(6 \pm 4) \times 10^{-4}$ n=4	85.7%
DB24C8 in CHCl_3	3.03×10^{-5}	2.52×10^{-4}	PFOSA	3.00×10^{-5}	$(5 \pm 3) \times 10^{-4}$ n=4	91.7%
Experiment not done in hexane because DB24C8 does not dissolve in hexane						
DC24C8 in CHCl_3	3.32×10^{-5}	2.52×10^{-4}			$(3 \pm 4) \times 10^{-2}$ n=4	87.3%

crown / solvent	moles of crown	moles of uranium	synergist	moles of synergist	D_U Average	mass balance
DC24C8 in CHCl ₃	3.32 x 10 ⁻⁵	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	(3.5±0.3) x 10 ⁻³ n=4	84.8%
DC24C8 in hexane	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴			(4±3) x 10 ⁻⁴ n=4	91.5%
DC24C8 in hexane	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	(2±1) x 10 ⁻⁴ n=4	87.7%
DC18C6 in CHCl ₃	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴			5.37 x 10 ⁻³ n=2	89.6%
DC18C6 in CHCl ₃	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	(3.6±0.6) x 10 ⁻³ n=4	84.4%
DC18C6 in hexane	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴			1.79 x 10 ⁻⁴ n=2	85.4%
DC18C6 in hexane	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	1.31 x 10 ⁻⁴ n=2	86.3%
18C6 in CHCl ₃	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴			1.91 x 10 ⁻³ n=2	85.0%
18C6 in CHCl ₃	4.09 x 10 ⁻⁶	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	3.43 x 10 ⁻³ n=2	85.0%
18C6 in CHCl ₃	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	2.81 x 10 ⁻³ n=2	77.8%
18C6 in hexane	4.09 x 10 ⁻⁶	2.52 x 10 ⁻⁴			No partitioning	76.1%
18C6 in hexane	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴			8.34 x 10 ⁻⁵ n=2	78.9%
18C6 in hexane	4.09 x 10 ⁻⁶	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	4.48 x 10 ⁻⁴ n=2	80.9%
18C6 in hexane	3.03 x 10 ⁻⁵	2.52 x 10 ⁻⁴	PFOSA	3.00 x 10 ⁻⁵	1.65 x 10 ⁻⁴ n=2	76.7%

crown / solvent	moles of crown	moles of uranium	synergist	moles of synergist	D_U Average	mass balance
DC18C6 in CHCl ₃	3.54E-05	2.52 x 10 ⁻⁴ pH-0.77			7.57E-03	
DC18C6 in CHCl ₃	3.54E-05	2.52 x 10 ⁻⁴ pH 3			8.22E-05	
DC24C8 in CHCl ₃	2.63E-05	2.52 x 10 ⁻⁴ pH-0.77			6.17E-03	
DC24C8 in CHCl ₃	2.63E-05	2.52 x 10 ⁻⁴ pH 3			7.39E-05	

3.3.1.3. Calixarene

Liquid-liquid extraction of uranium with calix[6]arene into hexane and CHCl₃ was attempted but was unsuccessful due to poor separation of the aqueous and organic phases which caused formation of an emulsified third phase known as “crud” in the uranium extraction industry.

3.3.2. Extraction of Uranium to Supercritical Carbon Dioxide

3.3.2.1. Calix[6]arene

Calix[6]arene was chosen as a ligand for the extraction of uranium from aqueous to scCO₂ phase. Although the extraction of uranium with calix[6]arene to scCO₂ at 40°C and 300 atm did not produce detectable levels of uranium in the collection vessel, when

the stainless steel cell was opened, a small amount of dark-orange compound was found to have formed on the inner surface of the lid. This substance proved to be the uranyl-calix[6]arene complex.

Calix[6]arene is a solid and therefore was dissolved in an organic solvent (CHCl_3) before being added to the cell. Since CHCl_3 was not to be a reagent in the experiment, the calixarene solution was dripped onto either the lid or the sides of the cell and the CHCl_3 was allowed to evaporate before the cell was closed and charged with scCO_2 . It was assumed that the calixarene would dissolve in the scCO_2 after pressurization of the cell and thus be removed from the interior surface of the cell. It is thought that the reason no uranyl-calixarene complex was found in the CO_2 collection vessel may be that the calixarene did not dissolve in the scCO_2 but remained on the surface where it had been applied. The complex was scraped off the side of the cell from the application site indicating that the uranyl ion had complexed *in situ* and remained bound to the interior surface of the cell.

Upon analysis by electrospray mass spectrometry, the calixarene ring (molecular weight $636.73 \text{ g mol}^{-1}$) was found to have opened and broken into chains containing different numbers of phenolic units held together by the methylene bridges of the ring. In some cases one methylene bridge on a terminal phenolic unit of the chain was retained, some fragments retained methylenes at both ends of the chain, and in some cases no terminal methylenes were retained as can be seen in Table 3.3-2. No uranyl ion (molecular weight 270) was seen to be associated with chains having fewer than six units and a six-unit fragment not associated with the uranyl ion appears at 637.1. The peak at 905.1 represents a ring that remained intact and was therefore able to retain the uranyl ion

i.e. this is the peak for the uranyl ion-calix[6]arene complex. See Appendix III for the mass spectra of the uranyl-calix[6]arene complex.

Table 3.3-2. Fragments produced when calix[6]arene-uranyl complex was examined by electrospray mass spectrometry.

m/z value	intensity	fragment	number of phenolic units	number of terminal methylene bridges
213.0	5.42		2	1
269.9	11.79	$\text{O}=\text{U}=\text{O}^{2+}$	0	0
331.1	1.23		3	2
425.1	5.28		4	1
543.2	3.26		5	2
637.1	4.90		6	1
905.1	0.90	complexed with $\text{O}=\text{U}=\text{O}^{2+}$	6	closed ring

3.4. Extraction of Uranium with Tributyl Phosphate and Supercritical Carbon Dioxide

As discussed in the introduction, the $\text{UO}_2\text{-NO}_3\text{-TBP}$ complex has the stoichiometry $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{ TBP}$. Meguro [95,96] has suggested that the complexation reaction takes place in the aqueous solution as

followed by partitioning of the complex into the scCO_2 phase. If this is the mechanism, we would expect the extent of the partitioning of the uranium to depend on the activity of the TBP in the aqueous phase.

Another possibility, however, is that complexation takes place at the interface between the aqueous and CO_2 phases, with the TBP in the scCO_2 phase responsible for formation of the complex

again followed by partitioning of the complex to the scCO_2 phase. If this is the mechanism, we would expect the extent of partitioning of the uranium to depend on the activity of TBP in the scCO_2 phase.

However, it is known, and is further demonstrated below, that nitric acid partitions to the scCO_2 phase as a complex with TBP, HNO_3TBP [43,45,46,50,54,

55,57,59,87,97,98,99,105,106,107,108,110,111,112]. Thus a third possible mechanism for the partitioning of uranium into scCO₂ involves the exchange of protons complexed in this manner with uranyl ions in the aqueous phase:

In this case, the partitioning of the uranium into the scCO₂ phase will depend on the activity of the HNO₃TBP complex. The complication is, of course, that the activity of this species will itself be a function of either the TBP_(aq) or TBP_(CO2) activity. To gain insight into the mechanism of partitioning, experiments were performed to determine the concentrations of uranium in both phases as well as [TBP]_(aq), [TBP]_(CO2), [H⁺]_(aq), and total [NO₃⁻] in the CO₂ phase (presumably in the forms of HNO₃TBP_(CO2) and UO₂(NO₃)₂·2TBP_(CO2)).

Experiments to determine the concentration of NO₃⁻, TBP and H⁺ in the aqueous phase at atmospheric pressure were carried out in a 100 mL volumetric flask containing 50 mL of 2.73 M nitric acid and those for the scCO₂ phase at high pressure in a 100 mL stainless steel high pressure cell containing 50 mL of 2.73 M nitric acid with the balance being filled with scCO₂. As required, TBP and uranium were added to the cell.

3.4.1. TBP Partitioning in the Extraction System

3.4.1.1. Solubility of TBP in 2.73 M Nitric Acid at Atmospheric Pressure

In order to determine the concentration of TBP in the acidic aqueous phase prior to pressurization, i.e. its solubility, an excess of TBP was added to 50 mL of 2.73 M nitric acid. After allowing sufficient time for equilibration (with stirring) and phase separation, the aqueous phase was analyzed for TBP. The solubility of TBP in 2.73 M nitric acid at atmospheric pressure was found to be $494 \pm 128 \mu\text{g mL}^{-1}$. The experiment was repeated with the addition of uranyl ion in two different concentrations to determine whether the presence of uranium would affect the concentration of TBP in the aqueous phase (see Table 3.4-1). It was thought that when uranium was added $[\text{TBP}]_{(\text{aq})}$ would decrease due to the uranyl complex partitioning to the liquid TPB phase.

Table 3.4-1. Solubility of TBP in 2.73 M nitric acid in the presence of, and without, the addition of uranyl nitrate at 23°C and atmospheric pressure.

contents of reaction vessel	average with standard deviation of $[\text{TBP}]_{(\text{aq})}$ at saturation
50 mL 2.73 M HNO_3 0.015 moles TBP	494 ± 128 , n=4
50 mL 2.73 M HNO_3 0.015 moles TBP 5.24×10^{-4} moles U	401 ± 104 , n=4
50 mL 2.73 M HNO_3 0.015 moles TBP 1.05×10^{-3} moles U	521 ± 135 , n=8

As Table 3.4-1 shows, it was not possible to determine if the addition of uranium to the solution had an effect on the solubility of TBP partly due to the associated uncertainty but also for the following reason. Theoretically, when uranium was added to the solution, the $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complex would have formed at the phase boundary between the aqueous phase and the liquid TBP layer and then partitioned to the TBP layer. TBP from the liquid layer would then partition to the aqueous phase to re-establish equilibrium. Thus the $[\text{TBP}]_{(\text{aq})}$ would not change with the formation of the complex and its partitioning to the pure TBP layer as is depicted below.

Figure 1.5-1. Schematic diagram of species present in acidic aqueous and liquid TBP phases.

3.4.1.2. The Partition Coefficient of TBP at High Pressure

The experiments detailed here were designed such that the volume of TBP placed in the cell would dissolve completely in the aqueous and scCO_2 phases to ensure that a

third TBP-rich phase would not form in the cell under any temperature and pressure conditions. According to Meguro [92] at densities above 0.3 g mL^{-1} , 0.015 moles TBP (the experimental quantity used) will dissolve in the scCO_2 phase (Figure 3.4-1). It is essential to have only two phases because it is not possible at high pressure to measure the concentration of the $\text{UO}_2\text{-NO}_3\text{-TBP}$ complex dissolved in a third phase without being sure that this phase actually exists.

Since the distribution coefficient of uranium must be dependent on the concentration of TBP in one phase or the other, the aqueous and CO_2 phase concentrations of TBP were studied at different temperatures and pressures.

TBP in the Aqueous Phase at High Pressure

Aqueous phase samples were withdrawn from the cell and, after liquid-liquid extraction, were analyzed by GC-FID. Each time an aqueous sample was withdrawn, a volume of pure scCO_2 corresponding to the sample volume entered the cell from the syringe pump which was being operated in the constant pressure mode. This dilution of TBP in the scCO_2 phase was accounted for in all concentration and partition coefficient calculations.

In the region above 0.6 g mL^{-1} it was found that the concentration of $[\text{TBP}]_{(\text{aq})}$ at constant temperature shows no change (within experimental uncertainty of 25%) as Figure 3.4-2 shows. It was also found that, at constant density, the $[\text{TBP}]_{(\text{aq})}$ increased with increasing temperature. Since the solubility of TBP in water is known to decrease with increasing temperature [113] (Figure 3.4-3), were the system ideal, it would be

Figure 3.4-1. Solubility of TBP (M) versus density scCO_2 [92] including experimental concentration of TBP in cell (black horizontal line) during partitioning experiments.

Figure 3.4-2. $[\text{TBP}]_{\text{aq}}$ versus density of scCO_2 for 40-70°C. (Experimental uncertainty is $\pm 25\%$).

Figure 3.4-3. Solubility of TBP in water versus temperature at atmospheric pressure [113].

expected that as the temperature in the cell increased, the concentration of TBP in the aqueous phase would decrease. The experimental results differ which is an indication of the non-ideality of the HNO_3 -TBP- CO_2 system. The region below 0.6 g mL^{-1} will be discussed later.

[TBP] in the scCO_2 Phase at High Pressure

Experimental results show that the isothermal concentration of TBP in the CO_2 phase of the HNO_3 -TBP- CO_2 system decreased as the density increased (Figure 3.4-4). This decrease was caused by dilution of the scCO_2 phase by neat CO_2 as was explained above. The fact that K_{TBP} was constant within experimental uncertainty in spite of a decrease in $[\text{TBP}]_{(\text{CO}_2)}$ indicates that TBP from the aqueous phase partitioned to the scCO_2 phase to re-establish equilibrium as the TBP in the scCO_2 phase was diluted.

Non-ideality

K_{TBP} for the HNO_3 -TBP- CO_2 system was measured as a function of temperature and density. Figure 3.4-5 shows the partition coefficient versus density of TBP in the 2.73 M HNO_3 - scCO_2 system. A trend can be seen in looking at temperature variation at constant density. As the temperature increases from 40°C to 70°C , the partition coefficient decreases. There are two unrelated principles responsible for this trend. First, as the temperature increases, the density of the scCO_2 decreases and thus its solvent power is decreased due to fewer available CO_2 molecules to solvate TBP molecules.

Figure 3.4-4. [TBP]_(CO₂) versus density of scCO₂ for 40-70°C. (Experimental uncertainty is $\pm 25\%$).

Figure 3.4-5. K_{TBP} versus density of $scCO_2$ for 40-70°C. (Uncertainty is $\pm 15\%$).

Second, the kinetic energy of the system increases with temperature and attractive interactions between the CO₂ and TBP molecules are more likely to be overcome.

In order to illustrate the underlying causes of the non-ideality of the HNO₃-TBP-CO₂ system, indications of which have been seen in ΔH and ΔS of solution of TBP in this system, a theoretical partition coefficient (representing an ideal system) of TBP between scCO₂ and water was determined at different densities using solubility data from the literature for TBP in scCO₂ [92] (Figure 3.4-1) and in water [113] (Figure 3.4-3). The comparison of the experimental [TBP] in scCO₂ and in water with the ratio of solubility of TBP in scCO₂ and water gives a visual indication of how non-ideal the HNO₃-TBP-CO₂ system is. This non-ideality appears to increase with increasing temperature. Figures 3.4-6 to 3.4-9 show that the experimental data are relatively consistent over the range of densities plotted whereas the ratio of solubilities increases with increasing density at all temperatures. It is interesting to note that at constant density K_{TBP} decreases as the temperature increases but the ratio of solubilities shows a slight increase as the temperature increases. These figures reflect the exothermic enthalpy of partitioning under experimental conditions as opposed to the endothermic theoretical enthalpy of partitioning using the ratio of solubilities that was discussed in section 3.1.3.2.

The figures show little overall variation in K_{TBP} with increasing density within experimental uncertainty, (the curve at 40°C shows more variation but this may be due to cell conditions particular to this temperature as there was frequently greater uncertainty associated with measurements taken at 40°C than at 50-70°C) but, in reality, the curves should be considered in two sections, one above the region around 0.6 g mL⁻¹ and a separate section below. The reason for this will be discussed later.

Figure 3.4-6. Comparison of experimentally derived [TBP] in scCO₂ and water, and the ratio of the solubilities of TBP in scCO₂ [92] and water [113] representing an ideal system at 40°C.

Figure 3.4-7. Comparison of experimentally derived $[\text{TBP}]$ in scCO_2 and water, and the ratio of the solubilities of TBP in scCO_2 [92] and water [113] representing an ideal system at 50°C .

Figure 3.4-8. Comparison of experimentally derived $[TBP]$ in $scCO_2$ and water, and the ratio of the solubilities of TBP in $scCO_2$ [92] and water [113] representing an ideal system at $60^\circ C$.

Figure 3.4-9. Comparison of experimentally derived $[TBP]$ in $scCO_2$ and water, and the ratio of the solubilities of TBP in $scCO_2$ [92] and water [113] representing an ideal system at 70°C.

After analyzing these TBP data and reading the primary literature on the subject, it became apparent that the experimental data do not agree with statements by Meguro *et al* [96] and Addleman and Wai [101] with respect to the location of the formation of the $\text{UO}_2\text{-NO}_3\text{-TBP}$ complex and the mechanism behind it. Both Meguro, and Addleman and Wai are quoted below.

Meguro *et al* state in [96]:

Extraction of Uranium(VI) in Nitric Acid Solution with Supercritical Carbon Dioxide Fluid Containing Tributylphosphate

“The overall reaction can be expressed by the following formula, which is identical to that confirmed in the conventional TBP-solvent extraction.

Here, K_{ex} denotes an extraction constant given by Eq. (3.4-5).

$$K_{\text{ex}} = \frac{[\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2]_{\text{SF}}}{[\text{U}]_{\text{aq}} [\text{TBP}]_{\text{SF}}^2 [\text{NO}_3^-]_{\text{aq}}^2} \quad (3.4-5)$$

The extraction reaction (3.4-4) involves at least three elemental processes as follows:

- (i) a distribution of TBP between aqueous and supercritical CO_2 phases,
- (ii) a formation of complex $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ in the aqueous phase, and
- (iii) a distribution of the complex between aqueous and supercritical CO_2 phases.

The K_{ex} is, therefore, formulated by Eq. (3.4-6),

$$\log K_{\text{ex}} = \log K_{\text{D,comp}} - 2 \log K_{\text{D,TBP}} + \log K_{\text{f}} \quad (3.4-6)$$

Where $K_{\text{D,comp}}$, $K_{\text{D,TBP}}$, and K_{f} are the distribution coefficient of the complex, the distribution coefficient of TBP, and the formation constant of the complex in the aqueous phase, respectively.”

Corresponding to (ii) above, this research suggests that the complex is not formed in the aqueous phase, but at the phase boundary, and therefore any distribution of the complex between the aqueous and supercritical CO₂ phases will be due to its partitioning into both phases from the interface.

Based on his hypothesis that the uranium complex forms in the aqueous phase, Meguro continues:

“The concentration of TBP distributing from the supercritical CO₂ phase into the aqueous phase decreases due to the increase of the solubility of TBP in the supercritical CO₂ phase with the increase of P_{ex} (the extraction pressure) which leads to the decrease of overall D with the increase of P_{ex} .”

Addleman and Wai state in [101]:

Distribution Coefficients of $UO_2(NO_3)_2 \cdot 2TBP$ in Supercritical Fluid CO₂ as Determined by On-line Resolved Laser Induced Fluorescence

“ D (distribution coefficient of uranium) was found to increase with temperature for the extraction of uranium with TBP modified ScF CO₂. So why does D increase rapidly with temperature? More data is needed to study and confirm the thermal mechanism(s) governing this extraction. However, existing data and knowledge does provide some insight into this extraction system.

Compound solubility can change dramatically with temperature in ScF CO₂ due to solute volatility and changing solvent strength. It is worth noting that D values always decrease with increasing ScF density, when either temperature or pressure is changed. Similar to the pressure dependence of D , a probable factor in the observed temperature behaviour may be due to a relative change in TBP solubility with temperature, between the two phases. It is reasonable to postulate that as temperature goes up (and ScF density falls) a larger portion of the TBP distributes into the aqueous phase allowing more uranyl complex to be formed and subsequently extracted.”

This research shows that the decrease in D_U in the region above 0.6 g mL⁻¹ density is caused by a decrease in the concentration of TBP in the scCO₂ phase not, as

Meguro *et al* and Addleman and Wai state, a decrease in the concentration of TBP in the aqueous phase.

Experiments to investigate the partitioning of uranium between CO₂ and the aqueous phase were carried out at four different temperatures (40-70°C) and at pressures ranging from 80 to 300 atm. These conditions produced densities of scCO₂ in the range of 0.2 to 0.9 g mL⁻¹

The analyses of these experiments are divided into two sections. The first part covers the behaviour of TBP and the associated uranium complex at scCO₂ densities greater than 0.6 g mL⁻¹ and the second part covers behaviours at densities less than 0.6 g mL⁻¹. The reason for this division is, in part, that Meguro's work only covers densities greater than 0.6 g mL⁻¹. (Other reasons will be discussed below.) I wish to both comment on his data, and to examine the behaviour of the TBP-uranium system at lower densities.

The region above 0.6 g mL⁻¹ scCO₂

Meguro states [95,96], and Addleman and Wai postulate [101] that the uranyl complex forms in the aqueous phase [95,96]. At 60°C and densities greater than 0.6 g mL⁻¹, his Meguro's data show that as the pressure (and thus the density) increases, the distribution coefficient, D_U , decreases (Figure 3.4-10). In agreement with Meguro, the experimental data in Figure 3.4-11 show a decrease in D_U for 40, 60, 70°C as the density of the scCO₂ increases in this region. (The curve at 50° C shows an increase near 0.7 g mL⁻¹, thought to be an artefact, but then follows the decrease seen at the other

Figure 3.4-10. D_U versus. density of scCO_2 at 60°C according to Meguro [96].

Figure 3.4-11. Isotherms for D_U versus density at 40 - 70°C. (Uncertainty is $\pm 16.0\%$.)

temperatures.) Notably, this decrease in D_U corresponds to a decrease in the $[TBP]_{(CO_2)}$ (Figure 3.4-4), not a decrease in $[TBP]_{(aq)}$ as Meguro states. Further evidence that the uranyl complex does not form in the aqueous phase can be seen in Figure 3.4-2 where $[TBP]_{(aq)}$ shows no decrease corresponding to the decrease in D_U discussed above.

K_{TBP} in the region of density $> 0.6 \text{ g mL}^{-1}$ (Figure 3.4-5) is very large (a maximum of 1129 on the 40°C curve and a minimum of 330 on the 70°C curve) and the virtually horizontal curves show that K_{TBP} is not highly dependent on the density of the CO_2 contrary to statements by both Meguro and Wai.

In summary, Wai states that D_U decreases with increasing density of scCO_2 at densities greater than 0.6 g mL^{-1} and that the change in TBP solubility between the two phases with increasing density results in a lower $[TBP]_{(aq)}$ which decreases the formation of the uranyl complex in the aqueous phase.

Wai's data show:

$$1. \quad p \uparrow \quad D_U \downarrow$$

He states: $[TBP] \uparrow \quad D_U \uparrow$

If pressure is increased: $[TBP]_{(CO_2)} \uparrow \quad [TBP]_{(aq)} \downarrow \quad D_U \downarrow$

Conclusion: Since D_U decreases as the pressure (and thus the density) of scCO_2 increases, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ forms in the aqueous phase.

$$2. \quad T \uparrow \quad D_U \uparrow$$

He states: $\rho \uparrow \quad D_U \downarrow$

If temperature is increased: $\rho \downarrow$ $[\text{TBP}]_{(\text{aq})} \uparrow$ $D_U \uparrow$

Conclusion: Since D_U increases as $[\text{TBP}]_{(\text{aq})}$ increases, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ forms in the aqueous phase.

Meguro states that D_U decreases with increasing density and that this decrease is due primarily to a increase in $K_{D,\text{TBP}}$. He argues that as the density increases, the $[\text{TBP}]_{(\text{CO}_2)}$ increases (due to higher solubility), and thus $[\text{TBP}]_{(\text{aq})}$ decreases. Since the complex forms in the aqueous phase, this decrease explains the decrease seen in D_U with increasing density.

Meguro's data show:

$$1. \rho \uparrow \quad D_U \downarrow$$

He states: $\rho \uparrow$ $[\text{TBP}]_{(\text{CO}_2)} \uparrow$ $[\text{TBP}]_{(\text{aq})} \downarrow$ $D_U \downarrow$

Conclusion: Since D_U decreases as $[\text{TBP}]_{(\text{aq})}$ decreases, $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ forms in the aqueous phase.

But data from this work show:

$$1. \rho \uparrow \quad [\text{TBP}]_{(\text{CO}_2)} \downarrow \quad D_U \downarrow$$

$$2. \rho \uparrow \quad [\text{TBP}]_{(\text{aq})} \text{ stays constant}$$

Conclusion: $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ forms in the scCO_2 phase.

The experimental data collected for this project do not support an increase in K_{TBP} with increasing density in the region above 0.6 g mL^{-1} . Our data show that K_{TBP} is constant (within experimental uncertainty) with increasing density (Figure. 3.4-5), that $[\text{TBP}]_{(\text{CO}_2)}$ is decreasing due to dilution of the scCO₂ phase with neat CO₂ (Figure 3.4-4) and that $[\text{TBP}]_{(\text{aq})}$ is constant (also within experimental uncertainty) (Figure 3.4-2). Since K_{TBP} is constant while $[\text{TBP}]_{(\text{CO}_2)}$ is decreasing, any decrease in $[\text{TBP}]_{(\text{aq})}$ must be greater than the decrease in $[\text{TBP}]_{(\text{CO}_2)}$. However, since K_{TBP} is so large, a decrease in aqueous phase TBP is insignificant with respect to the large decrease seen in scCO₂ phase TBP.

The observed decrease in D_U is a direct effect of the lower concentration of TBP in the CO₂ phase because a decrease in D_U must follow a decrease in TBP. It is thought that any decrease in TBP in the aqueous phase would be due to partitioning of TBP to the CO₂ phase to re-establish the equilibrium disturbed by the dilution of the CO₂ phase and is not due to uranyl complex formation since the concentration of uranium (10^{-3} M) is so low. It is the $[\text{TBP}]_{\text{CO}_2}$ that is the direct source of TBP used to form the uranyl complex.

As further proof that the formation of the uranyl complex does not take place in the aqueous phase, using the concentration of uranyl complex that was measured in the CO₂ phase, we would expect that the formation constant, K , when expressed as a quotient of complex in the CO₂ phase, and the uranyl ion in the aqueous phase plus nitrate and TBP in the appropriate phases (equation 3.4-7), would give a constant even at different pressures since we are assuming the concentration equals the fugacity, i.e. $\gamma=1$, for all species according to (equation 3.4-8).

$$K = \frac{[(\text{UO}_2)(\text{NO}_3)_2 \cdot 2(\text{TBP})]_{(\text{CO}_2)}}{[\text{UO}_2^{2+}]_{\text{aq}} [\text{NO}_3^-]_{(\text{aq OR CO}_2)}^2 [\text{TBP}]_{(\text{aq OR CO}_2)}^2} \quad (3.4-8)$$

Four combinations were considered:

(A): nitrate and TBP in the aqueous phase

$$K = \frac{[(\text{UO}_2)(\text{NO}_3)_2 \cdot 2(\text{TBP})]_{(\text{CO}_2)}}{[\text{UO}_2^{2+}]_{\text{aq}} [\text{NO}_3^-]_{(\text{aq})}^2 [\text{TBP}]_{(\text{aq})}^2}$$

(B): nitrate aqueous and TBP in the CO₂ phase

$$K = \frac{[(\text{UO}_2)(\text{NO}_3)_2 \cdot 2(\text{TBP})]_{(\text{CO}_2)}}{[\text{UO}_2^{2+}]_{\text{aq}} [\text{NO}_3^-]_{(\text{aq})}^2 [\text{TBP}]_{(\text{CO}_2)}^2}$$

(C): nitrate in the CO₂ phase and TBP aqueous

$$K = \frac{[(\text{UO}_2)(\text{NO}_3)_2 \cdot 2(\text{TBP})]_{(\text{CO}_2)}}{[\text{UO}_2^{2+}]_{\text{aq}} [\text{NO}_3^-]_{(\text{CO}_2)}^2 [\text{TBP}]_{(\text{aq})}^2}$$

(D): nitrate and TBP in the CO₂ phase

$$K = \frac{[(\text{UO}_2)(\text{NO}_3)_2 \cdot 2(\text{TBP})]_{(\text{CO}_2)}}{[\text{UO}_2^{2+}]_{\text{aq}} [\text{NO}_3^-]_{(\text{CO}_2)}^2 [\text{TBP}]_{(\text{CO}_2)}^2}$$

Table 3.4-2 was constructed using experimental concentrations of the TBP and NO₃⁻ in the appropriate phases.

Table 3.4-2. Comparison of different K values based on whether the NO_3^- and TBP are present in the CO_2 phase or the aqueous phase where A = $[\text{NO}_3^-]_{(\text{aq})}$ and $[\text{TBP}]_{(\text{aq})}$ aqueous; B = $[\text{NO}_3^-]_{(\text{aq})}$ and $[\text{TBP}]_{(\text{CO}_2)}$; C = $[\text{NO}_3^-]_{(\text{CO}_2)}$ and $[\text{TBP}]_{(\text{aq})}$; D = $[\text{NO}_3^-]_{(\text{CO}_2)}$ and $[\text{TBP}]_{(\text{CO}_2)}$. (All measurements taken at 50°C .)

pressure (atm)	(A) $[\text{NO}_3^-]_{(\text{aq})}$ $[\text{TBP}]_{(\text{aq})}$	(B) $[\text{NO}_3^-]_{(\text{aq})}$ $[\text{TBP}]_{(\text{CO}_2)}$	(C) $[\text{NO}_3^-]_{(\text{CO}_2)}$ $[\text{TBP}]_{(\text{aq})}$	(D) $[\text{NO}_3^-]_{(\text{CO}_2)}$ $[\text{TBP}]_{(\text{CO}_2)}$
80	2.369E-15	4.922E-21	7.519E-07	1.562E-12
100	5.911E-15	9.509E-21		
120	6.402E-15	1.349E-20	7.608E-08	1.603E-13
140	4.996E-15	1.532E-20		
160	1.079E-14	1.834E-20	8.531E-10	1.450E-15
180	8.056E-15	1.117E-20		
200	7.885E-15	1.242E-20	2.219E-10	3.495E-16
220	9.599E-15	1.206E-20		
240	1.002E-14	1.356E-20	2.079E-10	2.814E-16

Looking at the change in K with pressure, in column C, with K proportional to $[\text{NO}_3^-]_{(\text{CO}_2)}$ and $[\text{TBP}]_{(\text{aq})}$, K varies over three orders of magnitude; in column D, where K is proportional to $[\text{NO}_3^-]_{(\text{CO}_2)}$ and $[\text{TBP}]_{(\text{CO}_2)}$, K varies over four orders of magnitude, in column A, $[\text{NO}_3^-]_{(\text{aq})}$ and $[\text{TBP}]_{(\text{aq})}$, K varies by a factor of five but in column B $[\text{NO}_3^-]_{(\text{aq})}$ and $[\text{TBP}]_{(\text{CO}_2)}$, K varies only by a factor of four. Although not conclusive on its

own, $[\text{NO}_3]_{(\text{aq})}$ and $[\text{TBP}]_{(\text{CO}_2)}$ allows K to have the most constant value of any of the possible combinations.

The region below $0.6 \text{ g mL}^{-1} \text{ scCO}_2$

An examination of the experimental data for $[\text{TBP}]_{(\text{CO}_2)}$ at densities below 0.6 g mL^{-1} shows that in this region the $[\text{TBP}]$ is decreasing as density increases (Figure 3.4-4). At lower CO_2 densities (closer to and below the critical density of scCO_2 of 0.47 g mL^{-1}), the TBP- CO_2 solution is less ideal. Therefore it is necessary to consider the fugacity and not the concentration of $\text{TBP}_{(\text{CO}_2)}$ at densities in this region. As the density increases and the scCO_2 phase approaches ideal conditions, the fugacity of the TBP approaches its concentration.

Relating $[\text{TBP}]_{(\text{CO}_2)}$ to the extraction of uranium, we now need to examine the trend seen in Figure 3.4-11, how D_U changes with density. The equilibrium we are assuming is the following (3.4-9), with an equilibrium constant K (3.4-10)

where $(\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP})_{(\text{CO}_2)}$ is referred to as “cmplx”

$$K = \frac{f_{\text{cmplx}(\text{CO}_2)}}{a_{\text{UO}_2^{+2}(\text{aq})} f_{\text{TBP}(\text{CO}_2)}^2 a_{\text{NO}_3^-(\text{aq})}^2} \quad (3.4-10)$$

$$= \frac{[\text{cmplx}(\text{CO}_2)] \phi_{\text{cmplx}(\text{CO}_2)}}{([\text{UO}_2^{+2}(\text{aq})] \gamma_{\text{UO}_2^{+2}(\text{aq})}) ([\text{TBP}(\text{CO}_2)]^2 \phi_{\text{TBP}(\text{CO}_2)}^2) ([\text{NO}_3^-(\text{aq})]^2 \gamma_{\text{NO}_3^-(\text{aq})}^2)}$$

$$\text{but, } D = \frac{[\text{cmplx}(\text{CO}_2)]}{[\text{UO}_2^{+2}(\text{aq})]} \text{ (as measured)}$$

$$\text{thus, } D = K [\text{TBP}(\text{CO}_2)]^2 [\text{NO}_3^-(\text{aq})]^2 \frac{\gamma_{\text{UO}_2^{+2}(\text{aq})} \gamma_{\text{NO}_3^-(\text{aq})}^2 \phi_{\text{TBP}(\text{CO}_2)}^2}{\phi_{\text{cmplx}(\text{CO}_2)}}$$

but, $\gamma_{\text{UO}_2^{+2}(\text{aq})}$, $\gamma_{\text{NO}_3^-(\text{aq})}$, and $[\text{NO}_3^-(\text{aq})]$ are assumed to be constants since pressure should have little effect on aqueous activities

$$\text{thus, } D = K' [\text{TBP}(\text{CO}_2)]^2 \frac{\phi_{\text{TBP}(\text{CO}_2)}^2}{\phi_{\text{cmplx}(\text{CO}_2)}} \quad (3.4-11)$$

where K' is a combination of constant terms.

$f_{\text{cmplx}(\text{CO}_2)}$ = fugacity of TBP – uranyl complex in CO_2 phase

$a_{\text{UO}_2^{2+}(\text{aq})}$ = activity of UO_2^{2+} in aqueous phase

$f_{\text{TBP}(\text{CO}_2)}$ = fugacity of TBP in CO_2 phase

$a_{\text{NO}_3^-(\text{aq})}$ = activity of nitrate in aqueous phase

ϕ = fugacity coefficient

γ = activity coefficient

This predicts that the measured value of D will depend on the $[TBP]_{(CO_2)}$, as well as on the non-idealities of both the TBP and the complex in the CO_2 phase. At higher densities, where the fluid phase is not very compressible, the TBP and the complex will be close to ideality (i.e. their fugacity coefficients will be close to 1) and thus the value of D should be proportional to the concentration of TBP squared. At lower densities, the two species in the CO_2 phase become less ideal, and the value of D will be a function of both

$$[TBP_{(CO_2)}]^2 \text{ and of the ratio } \frac{\phi_{TBP_{(CO_2)}}^2}{\phi_{complex_{(CO_2)}}} \quad (3.4-12)$$

For this reason the value of D initially increases, then decreases with the density of the CO_2 phase.

The $[TBP]_{(aq)}$ is constant within experimental error over this range of densities. The curve at $60^\circ C$ in Figure 3.4-2 shows some scatter but overall there is little variation in $[TBP]_{(aq)}$.

Considering that the $[TBP]_{(CO_2)}$ is constantly decreasing with increasing density of CO_2 (Figure 3.4-4), it might be expected that D_U would also show a decrease at lower densities of CO_2 as was the case at densities of $CO_2 > 0.6 \text{ g mL}^{-1}$. However, Figure 3.4-11 shows an increase in D_U at lower densities. $scCO_2$ is a poor solvent at low densities simply because there is a shortage of CO_2 molecules to solvate the uranyl complex molecules. As the density increases, it becomes a better solvent and the concentration of uranyl complex in the $scCO_2$ phase increases.

3.4.2. Nitrate Partitioning in the Extraction System

To act as a blank, water was contacted with scCO₂ and [NO₃⁻]_(CO₂) was measured. No nitrate was found in the scCO₂ phase, as expected. The experiment was repeated with 2.73 M HNO₃ as the aqueous phase and, again, no nitrate was detected in the scCO₂ phase. It is therefore apparent that HNO₃ cannot partition into scCO₂ on its own, likely because of the extreme polarity difference between HNO₃ and CO₂.

TBP was then added to the system, and the experiment was repeated. In these experiments it was apparent that HNO₃ had complexed with the TBP and partitioned into the scCO₂. When the uranyl ion was added to the HNO₃-TBP-CO₂ system, nitrate again partitioned to the scCO₂ phase, presumably as both the HNO₃TBP complex and the uranyl ion complex, UO₂(NO₃)₂ · 2TBP.

Experiments were carried out to determine the quantity of nitrate that is carried to the scCO₂ phase as the two different complexes, HNO₃TBP and UO₂(NO₃)₂ · 2TBP. However, given the low concentration of uranyl ion (2×10^{-3} M) in comparison to nitric acid (2.73 M) in the cell, it was expected that, in spite of the partition coefficient for the UO₂-NO₃-TBP complex being two to three orders of magnitude greater than that of the HNO₃-TBP complex, the total nitrate concentration in the scCO₂ would be, in the most part, due to the HNO₃-TBP complex. It was also thought that, within the limitations of the detection method, the concentration of nitrate in the presence of uranium might be perhaps slightly greater than the concentration of nitrate in the CO₂ with no uranium present.

The HNO_3 -TBP complex, as expected, was found to be the main source of nitrate in the scCO_2 ("A" in Figure 3.4-12). When the concentration of nitrate associated with the nitric acid complex, "A", is added to the concentration of nitrate known to be present when the $\text{UO}_2\text{-NO}_3$ -TBP complex (two nitrates per uranyl ion) partitions to the scCO_2 phase under identical experimental conditions, it can be seen ("C" in Figure 3.4-12) that only approximately 15% of the nitrate is present in the scCO_2 phase as the $\text{UO}_2\text{-NO}_3$ -TBP complex.

The concentration of nitrate associated with both the HNO_3 -TBP complex and the $\text{UO}_2\text{-NO}_3$ -TBP complex in the scCO_2 phase was seen to increase with increasing density of scCO_2 (Figure 3.4-12). This is because, at higher densities, the scCO_2 became a better solvent based on the fact that there were more CO_2 molecules present with which the nitrate complexes could form attractive molecular interactions. The lower nitrate concentration at densities above 0.85 g mL^{-1} is due to the lower concentration of TBP in the scCO_2 phase (TBP is required in the formation of the HNO_3 -TBP complex).

3.4.3. Hydrogen Ion Partitioning in the Extraction System

As was previously discussed, in addition to the complexation of the uranyl ion with TBP, TBP is also known to form a complex with nitric acid as $\text{TBP(HNO}_3\text{)}$. Since the formation of this second complex, like the $\text{UO}_2\text{-NO}_3$ -TBP complex, consumes TBP and nitrate, the partitioning of the hydrogen ion must also be studied.

The hydrogen ion concentration in the acidic phase of a system containing 50 mL

Figure 3.4-12. $[\text{NO}_3^-]$ present in the scCO_2 phase as $\text{TBP}(\text{HNO}_3)$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complexes at 50°C . A: $[\text{NO}_3^-]$ as $\text{TBP}(\text{HNO}_3)$ complex; B: $[\text{NO}_3^-]$ as $\text{TBP}(\text{HNO}_3)$ complex + $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$ complex ; C: calculated total $[\text{NO}_3^-]$

2.73 M nitric acid, 2.66×10^{-4} moles uranium was measured before cell pressurization (at atmospheric pressure and temperature) through titration with sodium hydroxide and found to be 2.73 ± 0.02 M (Table 3.4-3). Upon addition of TBP to this solution, the hydrogen ion concentration decreased to 2.58 ± 0.01 M.

Table 3.4-3. Hydrogen ion concentration in 50 mL 2.73 M nitric acid and uranium showing the effect of the presence of TBP at 23°C/1 atm and 40°C/120 atm.

Density of scCO ₂	Temperature/ pressure / density	Cell contents	[H ⁺] (M)
	23 °C / 1 atm	50 mL 2.73 M HNO ₃ 1.33 x 10 ⁻⁴ moles U	2.73 ± 0 .02
	23°C / 1 atm	50 mL 2.73 M HNO ₃ 1.33 x 10 ⁻⁴ moles U 0.015 moles TBP	2.58 ± 0.01
0.726	40°C / 120 atm / 0.726 g mL ⁻¹	50 mL 2.73 M HNO ₃ 1.33 x 10 ⁻⁴ moles U 0.015 moles TBP	2.59 ± 0.16

A parallel experiment was carried out with 2.73 M HNO₃, uranyl ion and TBP at high pressure. The aqueous phase was sampled and the [H⁺] was found, within experimental error, to be identical to that of the unpressurized experiment in the presence of TBP (Table 3.4-3). This indicates that the partition coefficient for the HNO₃-TBP complex between nitric acid and TBP at atmospheric pressure is the same as it is between

nitric acid and the TBP-scCO₂ solution at high pressure (the density of the scCO₂ was 0.726 g mL⁻¹ for this experiment).

When the [H⁺]_(CO₂) was measured, it was expected to be equal to [NO₃⁻]_(CO₂) due to the necessity of charge balance. However, at the density of 0.726 g mL⁻¹ there were $(7.000 \pm 0.006) \times 10^{-3}$ moles of hydrogen ion and $(5 \pm 1) \times 10^{-4}$ moles of nitrate present in the scCO₂ phase showing that the concentration of H⁺ was an order of magnitude higher than the concentration of nitrate. The low concentration of nitrate may be explained through an examination of the collection method. scCO₂ was allowed to bubble through 5 mL of water causing both the dissolved complex and dissolved free TBP precipitate out of solution upon decompression. (CO₂ loses its solvent properties at atmospheric pressure.) Since TBP was observed on the surface of the water in the collection vessel and the nitric acid complex is soluble in TBP, nitrate bound up in the complex would have dissolved in the TBP and therefore would not be present in the water for analysis.

3.4.4. Uranium Partitioning in Extraction System

When extracting uranium from the nitric acid aqueous phase to the scCO₂ phase, HNO₃, TBP, and UO₃ were placed in the cell and it was charged with scCO₂. Although, given enough time, the contents of the cell would have reached equilibrium, stirring was used to shorten the equilibration time by increasing the interfacial area and allowing more diffusion per unit time. It was then necessary to allow the aqueous and CO₂ phases to separate. Experiments were performed using different stirring and phase separation times and it was determined that a five minute stirring period followed by five minutes for

phase separation gave a consistent distribution coefficient for uranium over a two hour period (Figure 3.4-13).

The distribution coefficients of uranium were determined by taking samples (approximately 1 mL each) of the aqueous phase and analyzing them for uranium by ICP-MS. As each sample was withdrawn from the cell, additional scCO₂ was forced into the cell by the syringe pump since the system was being operated in a constant pressure mode. This raised the possibility that distribution coefficients measured one after another might differ, since the relative volumes of the two phases were changing and since the total amount of uranium in the cell was decreasing. At several temperatures and pressures, the volume of the sample was varied over time and it was found that the sample volume did not affect the distribution coefficient of uranium. By keeping the sample volume consistent, the distribution coefficient of uranium was also monitored as the volume of the aqueous phase in the cell decreased with successive sampling and it was found that the aqueous volume had no effect on the distribution coefficient of uranium. In order to extract the UO₂²⁺ ion to a non-polar solvent such as CO₂, complexation is required and a number of components are needed to assemble the complex.

Figure 3.4-11 shows isotherms at 40-70°C for D_U (the partition coefficient of uranium between water and scCO₂) versus density of scCO₂. Three of these isotherms show the partition coefficient increasing to a maximum around 0.6-0.7 g mL⁻¹ scCO₂, followed by an abrupt decrease at higher density. The isotherm at 40°C does not reach a maximum because at 40°C there is no data at lower densities to outline a potential

Figure 3.4-13. D_U versus time at 40°C and 120 atm. The contents of the cell were stirred for five minutes then an additional five minutes were allowed for phase separation before each sample was taken.

maximum. However, the trend to decreasing distribution coefficients at high densities seen at 50 - 70°C is present at 40°C as well.

3.4.4.1. Comparison of Experimental Results with Literature Values

Figures 3.4-14 to 3.4-17 show a comparison of the experimental results of the determination of D_U by Meguro [100] and Wai [101] with the experimental results of this thesis. While Meguro's partition coefficients are higher than the experimental results at 40°C, there is good agreement at 50°C, 60°C, 70°C. However, Meguro's data are only at higher densities. Figure 3.4-15 shows that Wai's partition coefficients are lower than both Meguro's and the experimental results.

3.4.5. Separation of Uranium from Other Metals

To investigate the extraction of uranium under pseudo-natural conditions, specifically the selectivity of the extraction process for uranium, solutions of 600-700 ppm in 2.73 M HNO_3 of the following elements were prepared.

Boron(III) as H_3BO_3 (boric acid)

Chromium(VI) as Na_2CrO_4 (sodium chromate)

Iron(III) as $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (iron nitrate)

Molybdenum(VI) as $(\text{NH}_4)_2\text{MoO}_4$ (ammonium molybdate)

Thorium(IV) as $\text{Th}((\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (thorium nitrate)

Figure 3.4-14. Comparison of Meguro [100] and experimental results for D_U (partition coefficient of uranium into scCO_2) versus pressure at 40°C . (Uncertainties: Meguro 19 %, experimental data 6 %.)

Figure 3.4-15. Comparison of Meguro [100] and experimental results for D_U (partition coefficient of uranium into scCO_2) versus pressure at 50°C. (Uncertainties: Meguro 19 %, experimental data 6 %.)

Figure 3.4-16. Comparison of Meguro [100] and experimental results for D_U (partition coefficient of uranium into scCO_2) versus pressure at 60°C. (Uncertainties: Meguro 19 %, experimental data 6 %.)

Figure 3.4-17. Comparison of Meguro [100] and experimental results for D_U (partition coefficient of uranium into scCO_2) versus pressure at 70°C. (Uncertainties: Meguro 19 %, experimental data 6 %.)

Uranium(VI) as UO_3 (uranium trioxide)

In order to compare the TBP-uranium extraction into scCO_2 with the industrial extraction process, solutions containing 600-700 ppm of the six elements were extracted into Isopar-M. Table 3.4-4 shows the Method Detection Limit (or minimum reporting limit) for the analysis of these elements. From this point on, experiments containing all six elements are referred to as “multi” while single element experiments are “solo”. In the following tables, “< MDL” indicates that the ICP-MS was unable to detect the analyte at the extracted concentration; it is included for completion purposes only.

Table 3.4-4. Method detection limits for ICP-MS.

Analyte	Method detection limit ($\mu\text{g L}^{-1}$)
boron(III)	2
chromium(VI)	1
iron(III)	20
molybdenum(VI)	1
thorium(IV)	1
uranium(VI)	1

A major contributing factor to selectivity is the coordination number of the metal complex. In the case of the uranyl complex, $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{ TBP}$, TBP completes the

chelation sphere giving the complex a coordination number of 8 and thus shielding the charged ion from the non-polar CO_2 solvent. The molecular structure of $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}$ below shows the uranium atom surrounded by four oxygen atoms contributed by two nitrate anions and two phosphoryl oxygen atoms of the two TBP molecules. Metal complexes with coordination numbers of 7 have been shown to be less soluble in scCO_2 [103].

Molecular structure of $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}$ complex [112].

3.4.5.1. Boron and Iron

The concentrations of boron and iron in the scCO_2 phase were below the limit of detection in both scCO_2 and Isopar-M under all conditions. In the case of boron in particular, this selectivity is very important since, according to Table 1.5-1, ^{10}B has a neutron cross-section of 3835 barns.

3.4.5.2. Chromium

Table 3.4-5 shows that chromium was not extracted in significant concentrations into scCO₂ or Isopar-M in the presence of, or without, TBP.

Table 3.4-5. Extraction of chromium to scCO₂ and Isopar-M at 50°C.

Metals present in cell	Solvent	Density (g mL ⁻¹)	TBP present	D _{Cr}
chromium	scCO ₂	0.227		0.01
chromium	scCO ₂	0.227	yes	0.04
chromium	scCO ₂	0.584	yes	0.03
chromium	scCO ₂	0.727	yes	0.06
chromium, boron, iron, molybdenum, thorium, uranium	scCO ₂	0.227		0.03
chromium, boron, iron, molybdenum, thorium, uranium	scCO ₂	0.227	yes	< MDL
chromium, boron, iron, molybdenum, thorium, uranium	Isopar-M			0.05
chromium, boron, iron, molybdenum, thorium, uranium	Isopar-M		yes	0.05

3.4.5.3. Molybdenum

Table 3.4-6 shows that molybdenum was not extracted into scCO₂ or Isopar-M in significant concentrations in the presence of, or without, TBP.

Table 3.4-6. Extraction of molybdenum to scCO₂ and Isopar-M at 50°C.

Metals present in cell	Solvent	Density (g mL ⁻¹)	TBP present	D _{Mo}
molybdenum	scCO ₂	0.227		0.20
molybdenum	scCO ₂	0.584		0.31
molybdenum	scCO ₂	0.727		0.09
molybdenum	scCO ₂	0.727	yes	< MDL
molybdenum, boron, chromium, iron, thorium, uranium	scCO ₂	0.227		0.09
molybdenum, boron, chromium, iron, thorium, uranium	scCO ₂	0.727	yes	0.03
molybdenum, boron, chromium, iron, thorium, uranium	scCO ₂	0.883	yes	0.01
molybdenum, boron, chromium, iron, thorium, uranium	Isopar-M			< MDL
molybdenum, boron, chromium, iron, thorium, uranium	Isopar-M		yes	0.01

3.4.5.4. Thorium

Thorium was not extracted to either scCO₂ or Isopar-M in the absence of TBP.

Thorium was extracted to scCO₂ and Isopar-M in significant amounts when TBP was present in the system, both in the solo and multi experiments (Table 3.4-7).

Table 3.4-7. Extraction of thorium to scCO₂ and Isopar-M at 50°C.

Metals present in cell	solvent	density (g mL⁻¹)	TBP present	D_{Th}
thorium	scCO ₂	0.227		< MDL
thorium	scCO ₂	0.584		< MDL
thorium	scCO ₂	0.727		0.01
thorium	scCO ₂	0.883		0.02
thorium	scCO ₂	0.227	yes	0.36
thorium	scCO ₂	0.584	yes	0.55
thorium	scCO ₂	0.727	yes	0.44
thorium	scCO ₂	0.883	yes	0.18
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.227		0.05
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.584		0.12
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.727		0.21
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.883		0.13
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.727	yes	0.31
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.584	yes	0.35
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.727	yes	0.49
thorium, boron, chromium, iron, molybdenum, uranium	scCO ₂	0.883	yes	0.21

Metals present in addition to thorium	Solvent	Density (g mL⁻¹)	TBP present	D_{Th}
thorium, boron, chromium, iron, molybdenum, uranium	Isopar-M			0.60
thorium, boron, chromium, iron, molybdenum, uranium	Isopar-M		yes	0.52

3.4.5.5. Uranium

Experiments were carried out to extract uranium “solo” and “multi” to scCO₂ and to Isopar-M (Table 3.4-8). In the solo scCO₂ experiment, not surprisingly, no detectable uranium was found to have been extracted to the scCO₂ in the absence of TBP. The addition of TBP to the uranium-solo system produced distribution coefficients in the range of 1.0 to 3.1 for uranium-solo depending on the density of scCO₂ (Figure 3.4-18). Uranium was also extracted from acidified aqueous phase containing all six elements (boron, chromium, iron, molybdenum, thorium and uranium). The same figure shows a comparison between the uranium-solo and uranium-multi distribution coefficients with TBP in the system. The distribution coefficient of uranium in the TBP-CO₂ system was found to decrease in the presence of other elements. (Figure 3.4-18, Table 3.4-8). This may be due to suppression of the extraction of the uranyl complex to the scCO₂ phase by a thorium complex that has also partitioned or there may be interactions between the uranyl ion and other metal cations and anions in the aqueous phase preventing the uranyl ion from forming the complex at the phase boundary and partitioning.

Figure 3.4-18. Comparison of the distribution coefficients for uranium-solo and uranium-multi from 2.73 M HNO_3 to scCO_2 in the presence of, and without, TBP.

Table 3.4-8. Extraction of uranium to scCO₂ at 50°C, and Isopar-M.

Metals present in cell	Solvent	Density (g mL ⁻¹)	TBP present	D _{Mo}
uranium	scCO ₂			0
uranium	scCO ₂	0.227	yes	1.0
uranium	scCO ₂	0.402	yes	1.7
uranium	scCO ₂	0.584	yes	2.4
uranium	scCO ₂	0.682	yes	2.6
uranium	scCO ₂	0.727	yes	3.1
uranium	scCO ₂	0.767	yes	1.8
uranium	scCO ₂	0.794	yes	1.9
uranium	scCO ₂	0.814	yes	1.8
uranium	scCO ₂	0.833	yes	2.0
uranium	scCO ₂	0.852	yes	1.6
uranium	scCO ₂	0.869	yes	1.4
uranium	scCO ₂	0.883	yes	1.3
uranium, boron, chromium, iron, molybdenum, thorium	scCO ₂	0.227		0.02
uranium, boron, chromium, iron, molybdenum, thorium	scCO ₂	0.227	yes	0.22
uranium, boron, chromium, iron, molybdenum, thorium	scCO ₂	0.584	yes	0.25
uranium, boron, chromium, iron, molybdenum, thorium	scCO ₂	0.727	yes	0.26
uranium, boron, chromium, iron, molybdenum, thorium	scCO ₂	0.883	yes	0.76
uranium	Isopar-M			0.18
uranium	Isopar-M		yes	0.56

Elements present in cell	Solvent	Density (g mL ⁻¹)	TBP present	D _{Mo}
uranium, boron, chromium, iron, molybdenum, thorium	Isopar-M			0.01
uranium, boron, chromium, iron, molybdenum, thorium	Isopar-M		yes	0.02

The extraction of uranium from nitric acid aqueous phase to Isopar-M was investigated to compare the efficiency and selectivity of the scCO₂ method to the industrial method. The uranium-solo extraction to Isopar-M increased eight-fold when TBP was added to the system which is expected since this is the industrially-proven method of uranium extraction. In the uranium-multi extraction to Isopar-M with TBP (Figure 3.4-19), the distribution coefficient for uranium was at least an order of magnitude lower than that of the uranium-solo Isopar-M with TBP experiment (Table 3.4-8). This decrease in D_U mirrors the results of the decrease in uranium extraction between the solo and multi scCO₂ experiment, perhaps for the same reasons stated above.

Figure 3.4-20 shows that molybdenum were co-extracted into both scCO₂ and Isopar-M and chromium was co-extracted with Isopar-M but not scCO₂. Thorium was co-extracted with uranium at all densities of scCO₂ and also into Isopar-M. The mrtals solutions used in these experiments contained 600-700 ppm of all metal and it should be noted that thorium is present in the ore at approximately 1% of the uranium concentration. Therefore, under realistic conditions, the co-extraction of thorium is not as significant as Figure 3.4-20 indicates.

Figure 3.4-19. Comparison of distribution coefficients of uranium-multi from 2.73 M HNO_3 to scCO_2 and Isopar-M in the presence of, and without TBP.

Figure 3.4-20. Distribution coefficients for chromium, molybdenum, thorium and uranium from 2.73 M HNO₃ solution of six elements (boron and iron were not detected).

Figure 3.4-21 is a plot of D_U/D_{element} versus density of scCO_2 indicating at which densities of scCO_2 the extraction shows greatest selectivity of uranium in the presence of the other elements. The most favourable density is 0.883 g mL^{-1} for selectivity with respect to thorium and 0.727 g mL^{-1} is most favourable for selectivity with respect to chromium

Due to the fact that all samples had to be analyzed by a commercial lab at considerable expense, all multi- scCO_2 and Isopar-M experiments were performed and analyzed only once. The experiments need to be repeated to verify the results. Because thorium is not present in the raw ore at equal concentration to that of uranium (as was the case in the experimental conditions), Figure 3.4-21 may not be a realistic representation of the actual concentrations of thorium that would be present in the scCO_2 or Isopar-M after extraction. It does, however, indicate that neither solvent can selectively extract uranium in the presence of thorium.

Figure 3.4-21. D_U/D_{element} versus density of scCO_2 at 50°C .

4. Conclusions

Uranium is extracted from nitric acid-acidified water to supercritical carbon dioxide-tributyl phosphate (scCO₂-TBP) solution with distribution coefficients (D_U) in the range of 0.2 to 2.5. D_U is highly dependent on the density of the scCO₂ with the maximum extraction taking place in the range of 0.6 to 0.7 g mL⁻¹ for all temperatures measured (40-70°C). The formation of the uranium complex, $UO_2(NO_3)_2 \cdot 2TBP$, is dependent on the concentration of TBP in the scCO₂ phase. A decrease in D_U was seen to correspond to a decrease in the concentration of TBP in the scCO₂ phase in the density region above 0.6 g mL⁻¹. At these densities, the concentration of TBP in the aqueous phase was not seen to decrease as D_U decreased

TBP has very high partition coefficients between acidified aqueous phase and scCO₂, in the range of 240 to 1300, depending on the density of scCO₂. However, when partition coefficients calculated from the ratio of the concentration of TBP in the scCO₂ phase and the aqueous phase are compared to the ratio of the solubilities of TBP in pure scCO₂ and pure water (an ideal system), it becomes clear that the experimental system is non-ideal and that this non-ideality increases with temperature. Additionally, the enthalpy and entropy of solution of TBP in the experimental system were found to be negative at all densities tested (0.3 to 0.7 g mL⁻¹) whereas in an ideal system the calculated values of these thermodynamic properties are positive at these densities. This non-ideality is likely due to the increase in solubility of CO₂ in water with density. A second influencing factor could be the solubility of water in the scCO₂ phase.

During the extraction of uranium to scCO_2 , up to 92% of the nitrate present in the scCO_2 phase is in the form of a second complex, HNO_3TBP . Although HNO_3TBP has distribution coefficients two to three orders of magnitude lower than those of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$, depending on the density of the scCO_2 , HNO_3TBP was found to contribute most of the nitrate present in the scCO_2 phase due to the high concentration of H^+ and NO_3^- in the aqueous phase.

The distribution coefficient of uranium in an extraction system containing nitric acid acidified aqueous phase was superior to the industrially-used organic phase Isopar-M with TBP system. The distribution coefficient of uranium was only 0.56 in the Isopar-M-TBP system compared to 0.2 to 2.5 for the scCO_2 -TBP system. The selectivity of the scCO_2 system for uranium in the presence of other naturally-occurring elements (boron, chromium, iron, molybdenum, thorium) was also superior to the Isopar-M system. The ratio of uranium to thorium in the scCO_2 -TBP system was found to be 0.4:1 for densities of scCO_2 up to 0.727 g mL^{-1} with a large increase to 3.6:1 at density 0.883 g mL^{-1} . This same ratio in the Isopar-M-TBP system is very low at 0.04 to 1. The ratio of uranium to chromium extracted by Isopar-M was 0.47 to 1 whereas no chromium was seen to extract to scCO_2 .

The formation of a uranyl complex with calix[6]arene in the presence of scCO_2 at 40°C and 300 atm (density 0.921 g mL^{-1}) was confirmed by mass spectrometry but extraction to scCO_2 was not detected indicating that calix[6]arene is capable of both complexation and extraction of uranium but that the solubility of the complex in scCO_2 may be low.

5. References

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Appendix I. Density of scCO₂ at various temperatures and pressures.

T (°C)	p (atm)	p (psi)	density scCO₂ (g mL ⁻¹)	T (°C)	p (atm)	p (psi)	density scCO₂ (g mL ⁻¹)
40	80	1176	0.301	50	80	1176	0.227
40	100	1470	0.612	50	100	1470	0.402
40	120	1764	0.726	50	120	1764	0.584
40	140	2057	0.776	50	140	2057	0.682
40	160	2351	0.799	50	160	2351	0.727
40	180	2645	0.832	50	180	2645	0.767
40	200	2939	0.847	50	200	2939	0.794
40	220	3233	0.866	50	220	3233	0.814
40	240	3527	0.881	50	240	3527	0.833
40	260	3821	0.895	50	260	3821	0.852
40	280	4115	0.910	50	280	4115	0.869
40	300	4409	0.921	50	300	4409	0.883
T (°C)	p (atm)	p (psi)	density scCO₂ (g mL ⁻¹)	T (°C)	p (atm)	p (psi)	density scCO₂ (g mL ⁻¹)
60	80	1176	0.196	70	80	1176	0.177
60	100	1470	0.301	70	100	1470	0.253
60	120	1764	0.477	70	120	1764	0.353
60	140	2057	0.569	70	140	2057	0.463
60	160	2351	0.645	70	160	2351	0.55
60	180	2645	0.699	70	180	2645	0.615
60	200	2939	0.735	70	200	2939	0.664
60	220	3233	0.76	70	220	3233	0.698
60	240	3527	0.784	70	240	3527	0.727
60	260	3821	0.804	70	260	3821	0.752
60	280	4115	0.824	70	280	4115	0.775
60	300	4409	0.840	70	300	4409	0.794

Appendix II. Engineering Diagram of 100 mL Extraction Cell.

CHEMISTRY DEPARTMENT CARLETON UNIVERSITY
OTTAWA, ONTARIO, CANADA

NUMBER REQ. 1	DATE JUNE 30, 00	PART TITLE	REV
DWG BY L.L.B	SCALE NTS	HIGH PRESSURE CELL	
	DWG NO. CELL 001	MATERIAL STAINLESS STEEL	

Appendix III. Mass Spectra of Uranyl-calix[6]arene complex.