DOE-EMSP Project Final Report

Project Title: Solvent Effects on Cesium Complexation with Crown Ethers from Liquid to Supercritical Fluids

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Visiting scientists – Richard A. Porter, M.D. Samsonov

Publications Derived from the Project


Project Summary

Nuclear magnetic resonance (NMR) techniques were used to study crown ether-water interactions in solvents of low dielectric constants such as chloroform and carbon tetrachloride. Water forms a 1:1 complex with a number of crown ethers including 12-crown-4, 15-crown-5, 18-crown-6, dicyclohexano-18-crown-6, dichlohexano-24-crown 8, and dibenzl-24-crown-8 in chloroform. Among these crown ethers, the 18-crown-6-H2O complex has the largest equilibrium constant ($K = 545$) and 97% of the crown is complexed to water in chloroform. Addition of carbon tetrachloride to chloroform lowers the equilibrium constants of the crown-water complexes. The partition coefficients of crown ethers ($D = crown$ in water/crown in solvent) between water and organic solvent also vary with solvent composition. At room temperature, the $D$ value for 18-crown-6 is about 0.25 between water and chloroform and the value increases to 48 between water and carbon tetrachloride. NMR studies of cesium-crown ether-water interactions in chloroform in the presence of picric acid turned out to be complicated for spectral analysis. Some results were obtained but with large uncertainties. NMR studies of crown-water interactions in supercritical CO2 using a capillary tubing technique was also not successful due to experimental difficulties. Instead, Fourier-Transform Infrared (FT-IR) spectroscopy was used to study crown-water interactions in liquid and supercritical CO2 using a high-pressure view-cell with diamond windows.

FT-IR spectra of 18-crown-6-water and dicyclohexo-18-crown-6-water complexes in liquid and in supercritical CO2 were studies under various experimental conditions. Water forms a 1:1 complex with 18-crown-6 at low ligand concentrations and a 1:2 sandwich complex at high ligand concentrations. Spectral analysis indicates that the 1:1 complex has two forms, one with both hydrogen atoms of the H2O molecule bonded to the oxygen atoms of the host cavity and the other with only one hydrogen bonding between water and the cavity oxygen. The equilibrium constant of the single hydrogen bond 18-crown-6-H2O complex decreases from 21±2 to 13±1 L mol$^{-1}$ with an increase in temperature from 25 °C to 60 °C at 200 atm CO2. The equilibrium constant of the double hydrogen bond complex decreases from 14±2 to 2±1 from 25 °C to 60 °C under the same CO2 pressure. The enthalpies of the reaction for the single hydrogen bond and the double hydrogen bond complexes were determined to be -12±2 KJ mol$^{-1}$ and -38±3 KJ mol$^{-1}$, respectively. Density shows little effect on the equilibrium constants of the crown-water complex in supercritical CO2. The crown-water complex can be regarded as a Lewis acid-base complex with the crown being the electron donor and the water as the electron acceptor. This Lewis acid-base complex formation mechanism may provide a means of introducing insoluble hydrophilic acids into supercritical CO2 for chemical reactions and separations.

Several techniques were used to characterize complex formation between tri-n-butylphosphate (TBP) and some inorganic acids using NMR and other methods. TBP forms complexes with aqueous acids such as nitric acid and hydrochloric acid through hydrogen bonding of the electron donating P=O group. The Lewis acid-base complex has a general formula of TBP(acid)$_x$(H2O)$_y$, with $x$ and $y$ values depending on the relative amounts of TBP and acid used in the preparation. The $x$ and $y$ values can be determined by conventional titration methods. NMR spectra show that the protons of the acid and the water in the complex undergo rapid exchange resulting in a single resonance peak. The solubilities of some complexes such as TBP(HNO3)$_{0.5}$(H2O)$_{0.7}$ and TBP(HCl)$_{0.8}$(H2O)$_{2.8}$ are in the range of 1-2 mol% in supercritical CO2 at 40 °C and around 110 atm. When the TBP-nitric acid complex is added to the supercritical CO2, an anti-solvent effect of CO2 causes part of the acid in the complex to
precipitate out forming small droplets in the fluid phase. These small acid droplets may be highly effective for oxidization and dissolution of metals and oxides in supercritical CO2. Nitric acid and hydrochloric acid are normally not soluble in supercritical CO2. Using the Lewis acid-base complex formation mechanism with TBP as a carrier, these acids become soluble in supercritical CO2 because TBP is CO2-philic. This simple method of introducing acids into supercritical CO2 may have a wide range of applications for developing potential supercritical fluid processes.

One application of the TBP-nitric acid complex is for dissolution of uranium dioxide in supercritical CO2. Our study has shown that solid UO3 and UO2 powders can be dissolved in supercritical CO2 using a TBP-nitric acid complex such as TBP(HNO3)0.7(H2O)0.7. The dissolution of UO2 with the TBP-nitric acid complex in supercritical CO2 is particularly interesting because it may lead to the development of a dry and green process for treating UO2 contaminated wastes. The dissolution of UO2 probably involves oxidation of UO2 to uranyl ions (UO2)2+ followed by formation of the UO2(NO3)2(TBP)2 complex which is very soluble in supercritical CO2. Demonstration of this direct supercritical fluid dissolution process for treatment of uranium dioxide contaminated wastes and for reprocessing of spent nuclear fuels are current being conducted by the Nagoya University in collaboration with Japanese companies including Mitsubishi Heavy Industries, Japan Nuclear Cycle Corp and Kobe Steel.

This project has provided valuable opportunities for research as well as for education at the University of Idaho. Three graduate students, one undergraduate student, and two visiting scientists received financial support from the project for their research at the University of Idaho. The project has produced 6 journal publications plus an equal number of presentations at professional meetings.
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I. Introduction

Utilizing supercritical fluids as solvents for extraction, separation, synthesis, and cleaning has been a very active research area in the past two decades. The reasons behind this technology development are mainly due to the changing environmental regulations and increasing costs for disposal of conventional liquid solvents. Carbon dioxide is widely used in supercritical fluid extraction (SFE) applications because of its moderate critical constants ($T_c = 31.1 ^\circ C$, $P_c = 72.8$ atm, $\rho_c = 0.471$ g/mL), inertness, low cost, and availability in pure form. However, because CO$_2$ is a linear triatomic molecule (with no dipole moment), it is actually a poor solvent for dissolving polar compounds and ionic species. A method of dissolving metal ions in supercritical CO$_2$ was developed in the early 1990s using an in situ chelation technique. In this method, a CO$_2$-soluble chelating agent is used to convert metal ions into soluble metal chelates in the supercritical fluid phase. Quantitative measurements of metal chelate solubilities in supercritical CO$_2$ were first made by Laintz et al. in 1991 using a high pressure view cell and UV/Vis spectroscopy. In this pioneering study, the authors noted that fluorine substitution in the chelating agent could greatly enhance (by 2-3 orders of magnitude) the solubility of metal chelates in supercritical CO$_2$. A demonstration of copper ion extraction from solid and liquid materials using supercritical CO$_2$ containing a fluorinated chelating agent bis(trifluoroethyl)dithiocarbamate was reported in 1992. Since then, a variety of chelating agents including dithiocarbamates, $\beta$-diketones, organophosphorus reagents, and macrocyclic ligands have been tested for metal extraction in supercritical fluid CO$_2$. Highly CO$_2$-soluble metal complexes involving organophosphorus reagents have been found and reported in the literature. Recently, direct dissolution of metal oxides such as uranium dioxide and lanthanide oxides in supercritical CO$_2$ using a tri-$n$-butylphosphate-nitric acid complex as the extractant has also been demonstrated. These studies have greatly expanded potential uses of the supercritical fluid extraction technology for metal related applications.

The in situ chelation-SFE technique appears attractive for nuclear waste management because it can greatly reduce the secondary waste generation compared with the conventional processes using organic solvents and aqueous solutions. Other advantages of using the SFE technology for nuclear waste management include fast extraction rate, capability of penetration into small pores of solid materials, and rapid separation of solutes by depressurization. The tunable solvation strength of supercritical fluid CO$_2$ also allows potential separation of metal complexes based on their difference in solubility and partition between the fluid phase and the matrix.

This study started with a study of crown ether-water interactions in a water/organic solvent biphasic system. Proton nuclear magnetic resonance (NMR) spectroscopy was used as a probe to evaluate chemical environments and to calculate equilibrium constants of a number of crown ether-water complexes in chloroform (dielectric constant $\varepsilon = 4.8$ at 20 $^\circ C$) and in mixtures of chloroform and carbon tetrachloride ($\varepsilon = 2.2$ at 20 $^\circ C$). The partition coefficients of a number of crown ethers between water ($\varepsilon = 80.4$ at 20 $^\circ C$) and the organic solvents were also determined by the proton NMR technique. The results are given in a paper entitled “Partition Coefficients and Equilibrium Constants of Crown Ethers Between Water and Organic Solvents Determined by Proton Nuclear Magnetic Resonance” published by the Journal of Chemical and Engineering Data. NMR studies of cesium-crown ether-water interactions in chloroform in the presence of picric acid turned out to be complicated for spectral analysis. Some results were obtained but with large uncertainties. An approach to use a capillary tubing NMR technique to study crown ether-water interactions in supercritical CO$_2$ was also not successful because of experimental
difficulties. Finally, a Fourier-Transform Infrared (FT-IR) technique was chosen to study crown ether-water complexes with 18-crown-6 and with dicyclohexo-18-crown-6 as hosts in liquid and in supercritical CO$_2$. FT-IR spectroscopic evidence shows that water can form 1:1 and 1:2 (sandwich) complexes with 18-crown-6 in supercritical CO$_2$. In the 1:1 complex, H$_2$O can be bonded to the crown ether with one hydrogen bond or with both hydrogen atoms bonded to the oxygen atoms of the host cavity. The equilibrium constants of the 18-crown-6-water complex at different temperatures and pressures were measured. Density showed little change of the equilibrium constant. The enthalpies of formation of the crown-water complexes involving a single hydrogen bond and with two hydrogen bonds with the water molecule were also determined. The FT-IR results are published in a *Journal of Physical Chemistry* article entitled “An FT-IR Study of Crown Ether-Water Complexation in Supercritical CO$_2$.”

The crown-water complex in supercritical CO$_2$ can be considered a Lewis acid-base complex with crown ether acting as a Lewis base (electron donor) and water as a Lewis acid (electron acceptor). This Lewis acid-base complex formation mechanism may provide a method of introducing hydrophilic compounds such as water or water soluble acids in supercritical CO$_2$. An NMR study of some Lewis acid-base complexes of relevance to nuclear waste related problems was conducted. Tri-n-butylphosphosphate (TBP) was chosen as a Lewis base for this study because it is highly soluble in supercritical CO$_2$ and is known to form stable complexes with many metal species particularly lanthanides and actinides. TBP forms a 1:1 complex with water through hydrogen bonding with the electron donating P=O group of TBP. TBP also forms Lewis acid-base complexes with other hydrophilic acids such as nitric acid and hydrochloric acid in a general form (TBP)(acid)$_x$(H$_2$O)$_y$. These inorganic acids (i.e. aqueous nitric acid and hydrochloric acid) are not soluble in CO$_2$. Through hydrogen bonding, these acids can be dissolved in supercritical CO$_2$ using TBP as a carrier with solubilities typically in the order of 1-2 mol% in supercritical CO$_2$ at 40 °C and 110 atm. Some examples of the Lewis acid-base complex formation method for introducing hydrophilic acids in supercritical CO$_2$ are given in a paper entitled “Lewis Acid-Base Complex Formation for Dissolution of Acids in Supercritical Carbon Dioxide” submitted to *Chemical Communications* for publication. This method of dissolving acids in supercritical CO$_2$ may have a wide range of applications because acids are often needed for chemical reactions and separations in supercritical processes. The TBP-nitric acid complex was further characterized by other methods to evaluate their compositions and phase behavior in supercritical CO$_2$. The results of characterization of the complex are given in an article “Characterization of Tri-n-butylphosphosphate-Nitric Acid Complex – A CO$_2$-Soluble Extractant for Dissolution of UO$_2$” published in *Industrial and Engineering Chemistry Research*. One application of the TBP-nitric acid complex is for dissolution of metals and oxides in supercritical CO$_2$. Nitric acid is an oxidizing agent. It is known that concentrated nitric acid can oxidize solid uranium dioxide UO$_2$ to uranyl ions (UO$_2$)$^{2+}$. This reaction is important for dissolution of uranium dioxide in supercritical CO$_2$. For example, when a TBP-nitric acid complex dissolved in supercritical CO$_2$ is in contact with uranium dioxide, the acid can oxidize UO$_2$ to the uranyl ion followed by TBP coordination with the ion to form the UO$_2$(NO$_3$)$_2$(TBP)$_2$ complex. Based on our previous research, UO$_2$(NO$_3$)$_2$(TBP)$_2$ complex is one of the most soluble metal complexes known in the literature with a solubility around 0.45 mol L$^{-1}$ at 40 °C and 200 atm. The solubility of the complex increases with pressure at a given temperature. When the solubility of the complex is plotted against density of supercritical CO$_2$ in logarithmic scale, it shows a linear relationship. The ability of the TBP-nitric acid complex for direct dissolution of
uranium dioxide in supercritical CO₂ is described in a paper “Dissolution of Uranium Dioxide in Supercritical Fluid Carbon Dioxide” published in *Chemical Communication*. This supercritical fluid dissolution technique may lead to development of a dry process for treating uranium dioxide contaminated waste or even for possible recycling of spent nuclear fuels. Demonstrations of these possible applications are currently underway in Japan.

This project has provided opportunities for research as well as for education at the University of Idaho. Three graduate students received financial support from the project for their thesis research. One graduate student Xiang-Rong Ye completed his Ph.D. degree in chemistry at the University of Idaho last year. Other two graduate studies are expected to finish their Ph.D. degrees this year. An undergraduate student and two visiting scientists were also supported by this project. The project has produced 6 journal publications plus an equal number of presentations at professional meetings.

**References**
II. NMR Study of Crown Ether-Water Interaction

This project started with a study of crown ether-water interaction in a low dielectric constant solvent chloroform ($\varepsilon = 4.8$ at $20^\circ$C) using proton nuclear magnetic resonance (NMR) spectroscopy as a probe. The reason of studying crown-water interaction is that liquid-liquid extraction of metal species from aqueous solutions ($\varepsilon = 80.4$ for water at $20^\circ$C) is often done using an organic solvent with a low dielectric constant. Another purpose of this study is to determine the influence of solvent such as a mixture of chloroform and carbon tetrachloride on the crown-water interaction. The dielectric constant ($\varepsilon$) of CCl$_4$ is about 2.2 at $20^\circ$C.

Supercritical CO$_2$ has a small dielectric constant and the $\varepsilon$ value varies with density. For example, at $50^\circ$C and 200 atm, the dielectric constant of CO$_2$ is about 1.4. The organic solvent mixtures cover a wide range of solvent parameters which are comparable to those of liquid and supercritical CO$_2$ at different densities. Some crown ethers are appreciably soluble in water leading to their partitioning between the water and organic phases. NMR measurements also enable us to obtain partition coefficients of crown ethers between water and organic solvents. These data are very useful for solvent extraction of the alkali.

Proton NMR is a very precise analytical technique for measuring the amount and chemical environment of water in organic solvents. In the case of chloroform, a commercially available deuterated solvent CDCl$_3$ can be used as the solvent and proton resonance peaks of water bonded to a crown ether can be easily measured. The proton NMR spectra of unsubstituted crown ethers are simple because of their symmetrical molecular structure. Overlapping of crown ether proton resonance peaks with that of water complexed with the host molecule does not create a problem for NMR measurements. Typical NMR spectra of 18-crown-6 in the CDCl$_3$ phase after equilibration with water are shown in Figure 1. The spectra were obtained using a 500 MHz Bruker DRX500 spectrometer. The experimental details are given in our publication #1 “Partition Coefficients and Equilibrium Constants of Crown Ethers between Water and Organic Solvents Determined by Proton Nuclear Magnetic Resonance”.

Figure 1. Typical PNMR spectra of 18-crown-6 in the CDCl$_3$ phase, the concentration of 18-crown-6 after equilibration with water, from top to bottom: 0.00 M, 0.002 M, 0.075 M, 0.153 M and $\text{H}_2\text{O}$ resonance peak at 1.565, 1.874, 2.393, 2.668 ppm, respectively.
The 7.24 ppm proton resonance peak in Figure 1 is due to the small amount of CHCl₃ present in CDCl₃. Chemical shifts in the organic phase are calibrated by setting the chloroform chemical shift to this value. Water dissolved in chloroform has a proton resonance peak at 1.565 ppm. In the presence of a crown ether such as 18-crown-6, the water dissolved in chloroform can be bound to the crown ether to form a complex or exist as uncomplexed free water. 18-crown 6 has a single resonance peak for the ring protons at 3.65 ppm. The complexed H₂O and the free H₂O apparently undergo rapid exchange in the organic phase resulting in a single peak which shifts downfield as the crown ether concentration increases.

The equilibrium model for the partition of a crown ether (L) between water and chloroform and the formation of a crown-water complex (L•H₂O) in the organic phase is represented in detail in our publication #1. An outline of our experimental measurements and calculations to obtain the equilibrium constant of crown-water complexes in chloroform is given below. The equilibrium constant for the crown-water complex is defined as

\[ K = \frac{[L \cdot H_2O_{(org)}]}{[L_{(org)}][H_2O_{(org)}]} \]  \hspace{1cm} (1)

The fraction of crown molecules complexed to water is defined as

\[ k = \frac{[L \cdot H_2O_{(org)}]}{[L_{(org)}] + [L \cdot H_2O_{(org)}]} \]  \hspace{1cm} (2)

The k value can be determined from the total water \([H_2O_{(org)}]^0\) and total crown \([L_{(org)}]^0\) present in the organic phase (from NMR intensities) by the following equation

\[ [H_2O_{(org)}]^0 = k[L_{(org)}]^0 + [H_2O_{(org)}] \]  \hspace{1cm} (3)

From the k value, we can calculated the equilibrium constant by the following equation

\[ k = \frac{K[H_2O_{(org)}]}{1+K[H_2O_{(org)}]} \]  \hspace{1cm} (4)

From the NMR resonance peak shift (δ) of the H₂O peak, we can also calculate k and δ₀ (the chemical shift of free water in chloroform) and δ₁ (the chemical shift of complexed water in chloroform) using the following equation

\[ \delta = \delta_0 + k(\delta_1 - \delta_0) \frac{[L_{(org)}]^0}{[H_2O_{(org)}]^0} \]  \hspace{1cm} (5)

Figure 2 shows plots of experimental data based on equations (3) and (5) for 18-crown-6 in CDCl₃/H₂O system. Linear relationships are observed in these plots supporting the equilibrium assumptions made in this study.

Figure 2. Linear relationship between: (a) total water and 18-crown-6 concentration in chloroform; \(([H_2O_{(org)}]^0 = 0.9704[L_{(org)}]^0 + 0.0601; \text{ correlation coefficient } r = 0.9955) \) (b) observed chemical shift of water and the ratio \([L_{(org)}]^0/[H_2O_{(org)}]^0\) in chloroform (eq 5) \((\delta = 1.5015[L_{(org)}]^0/[H_2O_{(org)}]^0 + 1.5611; r = 0.9982).\)
Table 1 lists the equilibrium constants of various crown-water complexes in chloroform and in mixtures of chloroform and carbon tetrachloride determined by this study. The partition coefficient ($D = [L_{(aq)}]/[L_{(org)}]$) of various crown ethers between water and the organic solvent system determined by this NMR study are also given in the table.

In CDCl₃, the $k$ values for unsubstituted crown ethers 12C₄, 15C₅, and 18C₆ are 0.15, 0.54, and 0.97, respectively. This trend shows strong binding of water for 18C₆ relative to the smaller rings. Substitution in crown ethers tends to lower the $k$ value. Thus, for DCH18C₆, the $k$ value in chloroform is lowered to 0.70 compared with a value of 0.97 for the unsubstituted 18C₆. In the case of DCH24C₈ and DB24C₈, benzyl substitution further lowers the $k$ value compared with cyclohexyl substitution in 24C₈. The equilibrium constant ($K$) defined by eq 4 varies from 2.78 for 12C₄ to 545 for 18C₆ in chloroform. The $K$ value for the substituted (DCH18C₆) crown is much lower than that of the unsubstituted (18C₆) one (32 versus 545). The $\delta_0$ values for the three unsubstituted crown ethers are approximately constant (in the range of 1.53±0.04 ppm) as expected. Considering the experimental error the $\delta_1$ value is stable.

For the individual ligands, there are several clear trends with respect to the variation of solvent composition (CDCl₃+CCl₄). First, the amount of free water dissolved in the organic phase decreases with increasing CCl₄ fraction in the solvent. This is expected since decreasing the solvent polarity should result in lower solubility of water in the organic phase. In all cases, the parameter $k$ representing the fraction of ligand bound to water also decreases monotonically as the proportion of CCl₄ increases. Thus, decreasing solvent polarity also reduces water-crown complexation ($[L*H₂O_{(org)}]$), leading to lower $k$ values. This is probably caused by the combination of a lower solubility of free water in the organic phase and intrinsic solvation effects on the crown-water complex. The equilibrium constant $K$, which includes the concentration of unbound water and the ligand in the mixed organic phase, changes less and in an irregular fashion. Because both $[H₂O]_{org}$ and $[L]_{org}$ vary drastically with the solvent composition, the $K$ values defined by eq 4 are not as useful as the $k$ values for discussion in the CHCl₃+CCl₄ system. In the binary solvent systems, $[H₂O]_{org}$ decreases with increasing CCl₄ fraction whereas $[L]_{org}$ changes independently in the opposite direction, resulting in irregular trends for the $K$ values.

From the crown ether PNMR peak intensities in the organic and in the aqueous phase, we also calculated the partition coefficients $D = [L_{(aq)}]/[L_{(org)}]$ as shown in Table 1. The $D$ values for 12C₄ and 18C₆ between water and chloroform are around 0.25 and that for 15C₅ is somewhat lower. For the crown ethers that are appreciably soluble in water, the partition coefficients show that extraction into the aqueous phase increases exponentially as the organic solvent polarity decreases. In the case of 18C₆, the $D$ value starts at 0.25 in 100% CHCl₃ becomes 1.16 with a 50:50 mixture of CHCl₃ and CCl₄ and rises up to 48 for a 100% CCl₄ solution (Figure 3.). For the substituted crown ethers DCH18C₆, DCH24C₈, and DB24C₈, the $D$ values are below detection (<0.01) in the concentration range (0.06 to 0.2) mol L⁻¹. Partitioning of 18-crown-6 between water and various organic solvents has been determined by several different methods including gravimetric and conductivity measurements. PNMR actually provides a simple and rapid method for determination of crown ether partition coefficients between water and organic solvents. The $D$ values given in Table 1 represent the first systematic measurements of such data using a PNMR technique.
Table 1. Equilibrium and chemical shift parameters by various crown ethers.\(^a\)

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<th>Crown</th>
<th>% / vol CDCl(_3^b)</th>
<th>k (L.mol(^{-1}))</th>
<th>K [H(<em>2)O(</em>{org})](^c)</th>
<th>D ppm</th>
<th>(\delta_y) ppm</th>
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\(^a\)Typical statistical errors: k \(\pm 5\%\), K \(\pm 10\%\), [H\(_2\)O\(_{org}\)] \(\pm 0.003\) mol\(^{-1}\), D \(\pm 5\%\), \(\delta_0\) \(\pm 0.04\) ppm, \(\delta_1\) \(\pm 0.3\) ppm; \(^b\)Volume percentage of CDCl\(_3\) in CCl\(_4\); \(^c\)Concentration in mol L\(^{-1}\); \(^d\) \(<0.01\) for the ligand concentration range 0.02-0.2 mol L\(^{-1}\)

NMR studies of crown-water complexation in liquid and in supercritical fluid CO\(_2\) were carried out at PNNL using a capillary tubing technique developed by Dr. Clem Yonker. The results were not reproducible because of slow diffusion of crown ether and water in capillary tubing to reach equilibrium. Another spectroscopic technique Fourier Transform Infrared (FTIR) spectroscopy was chosen to study crown-water complexation in supercritical CO\(_2\) using a high-pressure view-cell with diamond windows available in John Fulton’s lab at PNNL. The results are described in the next section.
III. FTIR Study of Crown Ether-Water Complexation in Supercritical Carbon Dioxide

Supercritical fluids have unique properties that make them highly attractive for extraction of metal ions from liquid and solid materials. Carbon dioxide is most widely used for supercritical fluid applications because of a number of advantages including (i) low toxicity, (ii) environmentally benign, (iii) low cost, (iv) moderate critical constants \( T_c = 31 \, ^\circ C \) and \( P_c = 73.7 \) bar, and (v) tunable solvation strength that varies with density. Selective extraction of metal species using a non-polar solvent such as \( \text{CO}_2 \) requires special chelating agents that should possess ion recognition ability and be soluble in supercritical fluid carbon dioxide (SF-CO\(_2\)).

Crown ethers have been extensively used for extraction of alkali metal and alkaline earth metal cations from aqueous solutions into organic solvents. For the extraction of metal ions from aqueous solutions using ligands dissolved in SF-CO\(_2\), the fluid phase will be saturated with water. Thus, water interaction with the ligand in the fluid phase plays an integral role in the extraction process. It has been reported that the extraction efficiency of alkali metal ions in conventional solvent processes depends on the solubility of water in the organic phase using macrocyclic polyethers as a complexing agent. With crown ethers, both computational simulation and spectroscopic studies show that in organic solvents, the water can bond to a macrocyclic host molecule by two different types of hydrogen bonding. The first type comprises of a single hydrogen bond between one hydrogen atom of a water molecule and one oxygen atom of the crown ether cavity. In this case, the water molecule is mostly located outside the cavity. The second type occurs inside the cavity and is composed of a water molecule bridging between two different oxygen atoms of the crown cavity.

FT-IR is a sensitive and qualitative technique that has been used during the past years to study hydrogen bonding in different solvents. For example, Fulton et al. used this technique to explore hydrogen bonding of methanol dissolved in supercritical carbon dioxide and found that a weak interaction between carbon dioxide and methanol significantly reduced the amount of methanol-methanol hydrogen bonding. Johnston et al. used it to understand the solvent effect on hydrogen bonding in supercritical fluids. They were able to determine, with a good accuracy, the
equilibrium constants and other thermodynamics data for the hydrogen bond between methanol and triethylamine. The FT-IR technique has also been used by Moyer et al. to determine how water is bonded to crown ethers in carbon tetrachloride. These authors assigned vibrational bands to free water and to two different kinds of hydrogen bonds mentioned above. In this report we examine the interactions of water and 18-crown-6 in liquid and supercritical CO₂ for the purpose of establishing a basis for using this green solvent in extraction processes utilizing crown ethers as extractants.

The details of the FTIR measurements of crown-water complexation are given in our publication #2 entitled “An FTIR Study of Crown-Water Complexation in Supercritical CO₂” published in the Journal of Physical Chemistry A (2003, 107, 11239-11244). According to our spectroscopic analysis, 18-crown-6 can form 1:1 complex or 2:1 complex with water in liquid and in supercritical carbon dioxide. According to our FTIR analysis, the 1:1 crown-water complex has two forms, one with H₂O located on top of the cavity with both of the hydrogen atoms bonded to the oxygen atoms of the crown ether (bridge bonding) and the other form involves only one hydrogen bond of the H₂O molecule with the crown cavity (single bondig). The structures of these crown-water complexes are illustrated in Figure 4.

![Figure 4. Schema of the three possible bonding between D₂O and 18-Crown-6. a) Bridge bonding; b) single bonding; c) a 1:2 complex in a sandwich configuration.](image)

A typical FTIR spectrum of free and bonded D₂O with 18-crown-6 in liquid CO₂ in supercritical CO₂ is shown in Figure 5. Peaks for the free D₂O, i.e. D₂O dissolved in SF-CO₂ without the crown ether, (O-D stretching, asymmetric at 2761 cm⁻¹ and symmetric at 2654 cm⁻¹) can be easily discerned and their positions are in agreement with those reported for D₂O molecules in the vapor (i.e. 2789 and 2666 cm⁻¹ for the D₂O vapor). The shifts of the D₂O vibrational stretchings to lower wave numbers in SF-CO₂ relative to single molecules in the vapor phase reflect the interactions of D₂O molecules with CO₂ in the fluid phase. When 18-crown-6 was added to the CO₂ solution, three other peaks at 2733, 2679 and 2590 cm⁻¹ appeared. According to the order of peak assignment of H₂O/18-crown-6 complex in carbon tetrachloride, the broad peak at 2590 cm⁻¹ should correspond to the symmetrical stretch of the O-D bond involved in the two hydrogen bond bridge as illustrated in Figure 4a. The D₂O molecule with one hydrogen bonding to the cavity oxygen is expected to have two stretching bands. The sharp O-D
band at 2733 cm$^{-1}$ should be the unbounded O-D stretching marked as 2 on Figure 5b. The bonded O-D stretching band (marked as 1 on Figure 4b) was assigned to the 2679 cm$^{-1}$ peak, located between the symmetrical and the asymmetrical stretching bands of free water. In the FT-IR spectra of H$_2$O/18-crown-6 complex in CCl$_4$, the bonded O-H stretching band was found at a lower energy than the symmetrical stretch band of free water. We confirmed our assignment of this bonded O-D band by completing two secondary experiments. One experiment was a comparison of the FTIR spectra of 18-crown-6/H$_2$O and 18-crown-6/D$_2$O complexes in CCl$_4$. We confirmed the peak assignment of the former as reported in the literature and the D$_2$O isotopic effect altered the peak order of the latter as shown in Figure 5. In another experiment, we confirmed that the order and assignment of the various O-D bands in 18-crown-6/D$_2$O complex in SF-CO$_2$ was the same in both CCl$_4$ and liquid CO$_2$.

When the 18-crown-6 concentration exceeds 0.4 mol L$^{-1}$ with a lower water concentration (less than 17 mmol L$^{-1}$), only one absorption band at 2590 cm$^{-1}$ is observed (Figure 5). All the D$_2$O molecules seem to be bridge bonded to the crown ether. This observation may be explained by the formation of a 1:2 complex between D$_2$O and 18-crown-6 as illustrated in Figure 4c. The O-D stretching band for this kind of complex should appear at the same frequency as the bridged form of D$_2$O (Figure 4a configuration). Our suggestion of an 1:2 complex formation is based on the assumption that by increasing the crown ether to water ratio in SF-CO$_2$, we should not change the equilibrium between D$_2$O molecules bonded to one oxygen atom (configuration 1b) or to two oxygen atoms (configuration 1a) of the cavity. As the concentration of 18-crown-6 in the system increases, it is conceivable that the single bonded D$_2$O molecule (configuration 1b) would form hydrogen bonding with another crown molecule via the unbounded O-D thus leading to the formation of an 1:2 complex. The law of mass action should favor the shifting of equilibrium from a 1:1 complex to a 1:2 complex between water and 18-crown-6 in SF-CO$_2$. Also in figure 3c, we show, for comparison, spectra of the double bond area of 18-crown-6 (at 0.041 M and 0.123 M) and D$_2$O (0.049 M) at 400 bar and 40 °C. Peaks occur at the same position for both the dimer and the monomer forms.
The formation of a 1:1 complex between 18-crown-6 and D$_2$O in the CO$_2$ phase at lower crown to D$_2$O molecular ratio was evaluated by the analysis of the FT-IR data and the equilibrium relations of the following equations:

$$18\text{C6} + D_2O \rightleftharpoons 18\text{C6} \cdot D_2O^{\text{single}}$$  \hspace{1cm} (6)

$$K_s = ([18\text{C6} \cdot D_2O^{\text{single}}]) / ([18\text{C6}][D_2O])$$

$$18\text{C6} + D_2O \rightleftharpoons 18\text{C6} \cdot D_2O^{\text{bridge}}$$  \hspace{1cm} (7)

$$K_b = ([18\text{C6} \cdot D_2O^{\text{bridge}}]) / ([18\text{C6}][D_2O])$$

Where $K_s$ and $K_b$ represent the equilibrium constants for the 1:1 complex with a single hydrogen bond (configuration 4b) and double hydrogen bonds (configuration 4a), respectively. The details are given in our publication #2.

The $K$ values vary considerably with CO$_2$ density. At a constant pressure (200 bar), the $K_s$ value decreases from 21±2 to 13±1 L mol$^{-1}$ with increase in temperature from 25 to 60 °C. The variation of $K_s$ with temperature is even greater for the same pressure, its value varies from 14±2 to 2±1 L mol$^{-1}$ from 25 to 60 °C. These $K$ values are comparable to the one reported by Moyer et al. (i.e. 15.6 (1.2) L mol$^{-1}$) for the 18-crown-6/H$_2$O complex in carbon tetrachloride. This implies that, in terms of hydrogen bonding between water and 18-crown-6, supercritical CO$_2$ behave as a non-polar solvent such as CCl$_4$ and not like chloroform. The $K$ value of 18-crown-6/H$_2$O complex in chloroform was reported to be 20 times larger than that in CCl$_4$. The influence of density (increase in pressure from 200 to 400 bar) at a constant temperature (i.e. 40 °C) on the two equilibrium constant $K_s$ and $K_b$ is shown on Figure 6. An increase in density causes a decrease in the $K_s$ and $K_b$ values.
The molar enthalpy of a hydrogen bonding ($\Delta H_i$) can be determined from the equilibrium constant at constant pressure by equation (4) from well known thermodynamic relations (equations 3), where $T$ is the absolute temperature in Kelvin and $R$ the ideal gas constant.

$$\left( \frac{\partial (\Delta G_i)}{\partial T} \right)_p = -\Delta S_i = \frac{\Delta G_i}{T} - \Delta H_i$$ and $$\Delta G_i^\circ = -RT \ln K_i$$ (7)

$$\left( \frac{\partial (\ln K_i)}{\partial 1 / T} \right)_p = -\frac{\Delta H_i}{R}$$ (8)

Using a linear regression on the plot of $\ln K$ versus $1/T$ (Figure 6), and assuming that $\Delta H$ is independent of temperature and density, the $\Delta H_i$ (for single hydrogen bond, configuration 1b) was found to be $-12\pm2$ kJ mol$^{-1}$ and $\Delta H_b$ (for bridge bonding, configuration 1a) to be $-38 \pm 3$ kJ mol$^{-1}$, both at 200 bar. The complexation process is exothermic as expected for a hydrogen bonding and its value is similar to the literature values for hydrogen bonding processes in both liquid solvents and in supercritical fluids. The fact that the hydrogen bonding process is exothermic and that the bonded species are more entropically ordered explain the decrease of $K$ values with the increase of temperature.

![Figure 6](image)

Figure 6. Left: density effect on equilibrium constants $K_a$ (●) and $K_b$ (○); Pressure varies from 200 to 400 bar at constant temperature (40°C); [18C6] = 41 mmol L$^{-1}$; [D$_2$O] = 49 mmol L$^{-1}$; Right: concentration of the two isomers (i.e. single (●) and double bond (○) between D$_2$O (49 mmol L$^{-1}$ total concentration in CO$_2$) and the 18-crown-6 (83 mmol L$^{-1}$ total concentration in CO$_2$) versus temperature (in Celsius).

The study has demonstrated that FT-IR is a sensitive technique for studying crown ether and water interactions in SF-CO$_2$. The O-D stretching vibrations for D$_2$O dissolved in SF-CO$_2$ show slight shifts to lower wave numbers relative to those found for D$_2$O in its vapor phase indicating interactions (salvation) of CO$_2$ with D$_2$O molecules in the supercritical fluid phase. In
the presence of 18-crown-6, D$_2$O forms a 1:1 complex with the macrocyclic molecule with two different configurations. The D$_2$O molecule can form one hydrogen bond with an oxygen atom of the crown cavity or it can be bonded to two oxygen atoms of the cavity in a bridged configuration. The equilibrium constant of the single hydrogen bond configuration is slightly greater than the two hydrogen bond configuration and both equilibrium constants decrease with increasing temperature. The enthalpy of the complex formation is -12±2 kJ mol$^{-1}$ for the former and -38±3 kJ mol$^{-1}$ for the latter. These values are within the range of hydrogen bonds reported in liquid solvents. At high 18-crown-6 to D$_2$O ratios, formation of an 1:2 complex in SF-CO$_2$ that involves one D$_2$O molecule hydrogen bonded to two crown ether molecules becomes possible.

IV. Lewis Acid-Base Complex Formation Mechanism for Dissolving water and acids in Supercritical Carbon Dioxide

The crown ether-water complex formation discussed in the previous sections involves hydrogen bonding between the crown ether oxygen atoms (electron donor) and the hydrogen atoms (electron acceptor) of the H$_2$O molecule. This type of complex can be considered a Lewis acid-base complex with crown ether acts as a Lewis base and water as a Lewis acid. The Lewis acid-base complex formation mechanism may provide a means of dissolving normally insoluble or slightly soluble hydrophilic compounds such as water in supercritical CO$_2$. This complex formation mechanism should not be limited to crown ethers as the Lewis base and water as the Lewis acid. Other compounds such as tri-n-butylphosphate with an electron donating P=O group may also be an effective Lewis base for introducing water and acids in supercritical CO$_2$.

Supercritical fluid processing has been a burgeoning area of research in recent years for both theoretical and practical considerations. Carbon Dioxide is the most widely used gas for supercritical fluid applications because of its moderate critical constants, nonflammable nature and environmental acceptability. However, since CO$_2$ is non-polar and has a low dielectric constant, supercritical CO$_2$ processing is limited by its poor ability to dissolve hydrophilic species. Several strategies have been developed in the past to make supercritical CO$_2$ more “solute-philic” including modifying CO$_2$ with polar solvents, utilizing water-in-CO$_2$ microemulsions, and complex formation approaches. Recently, dissolution of hydrophilic metal species in supercritical CO$_2$ has gained increasing attention because of potential applications in nuclear waste treatment, environmental remediation, semiconductor devices manufacturing, and chemical catalysis. The in situ chelation method for dissolving metal species in supercritical CO$_2$ developed by our research group in the early 1990s is widely used today for chemical and environmental studies. Several previous reports have demonstrated that the solubility of metal chelates in supercritical CO$_2$ can be significantly enhanced using CO$_2$-philic ligands such as fluorinated chelating agents and organophosphorus ligands. Among these reagents, tri-n-butylphosphate (TBP) is particularly interesting because it is a CO$_2$-philic Lewis base and is capable of forming stable coordination compounds with Lewis acids through the electron donating P=O group. The Lewis acid-base complex formation mechanism provides a simple method of dissolving hydrophilic acids in supercritical CO$_2$ using TBP as a carrier. This technique may have a wide range of applications in developing CO$_2$-based processes because acids are often needed for chemical reactions and separations. For this reason, we investigated Lewis acid-base complex formation with TBP as a carrier and measured the solubilities of some TBP-acid complexes in supercritical CO$_2$.

The complexes used in this study were prepared by shaking 5 mL of TBP (Avocado, Alfa Aesar, Ward Hill, MA) with a certain amount of an acid in a capped vial for one hour. Concentrated
nitric acid (15.5 M, Fisher, Fair Lawn, NJ), hydrochloric acid (37.4%, Fisher), and benzoic acid (Fisher) were used as received for this study. After shaking, the mixture was centrifuged for one hour and the TBP phase was removed for characterization. The acid content in the TBP phase was determined by diluting 1 mL of the TBP phase with 40 mL of water followed by NaOH (0.1 M) titration of the acid in the aqueous phase. The water content of the TBP phase was determined by Karl-Fischer titration. The TBP-acid complex has a general composition of TBP (Acid)$_x$ (H$_2$O)$_y$ with x and y depending on the relative amount of TBP and the acid used in the preparation. Examples of TBP-nitric acid and TBP-hydrochloric acid complexes are given in Table 1. The TBP-benzoic acid complex was prepared by dissolving a certain amount of solid benzoic acid in TBP directly. Because benzoic acid does not contain water the complex has a formula of TBP (Acid)$_x$.

Table 2. Compositions of some TBP-acid complexes prepared for this study

<table>
<thead>
<tr>
<th>Initial TBP/Acid Mixture</th>
<th>Composition of TBP-Acid Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mL TBP + 0.82 mL nitric acid (15.5 M)</td>
<td>TBP(HNO$<em>3$)$</em>{0.7}$(H$<em>2$O)$</em>{0.7}$</td>
</tr>
<tr>
<td>5 mL TBP + 1.3 mL nitric acid (15.5 M)</td>
<td>TBP(HNO$<em>3$)$</em>{1.0}$(H$<em>2$O)$</em>{0.4}$</td>
</tr>
<tr>
<td>5 mL TBP + 1.5 mL hydrochloric acid (12.3M)</td>
<td>TBP(HCl)$_{0.8}$(H$<em>2$O)$</em>{2.8}$</td>
</tr>
<tr>
<td>5 mL TBP + 2 g benzoic acid</td>
<td>TBP(benzoic acid)$_{0.5}$</td>
</tr>
</tbody>
</table>

Proton NMR spectra of a typical TBP-hydrochloric acid complex and a TBP-nitric acid complex are given in Figure 1. The spectra were taken using a 300 MHz (Bruker) spectrometer at room temperature. In the NMR measurement of pure complexes, deuterated water was placed in an insert and fitted into an NMR tube containing a TBP-acid complex. The purpose of the D$_2$O insert was to lock the NMR. A trace amount of HDO present in the deuterated water allows calibration of the instrument. TBP is known to form a 1:1 complex with H$_2$O and the TBP-H$_2$O complex has a single resonance peak at about 3.9 ppm. The proton NMR spectrum of the TBP(HCl)$_{0.8}$(H$_2$O)$_{2.8}$ complex shows a single peak around 10 ppm indicating the protons of H$_2$O and HCl in the complex undergo rapid exchange (Figure 1a). The other 4 peaks below 4 ppm are the protons from the butyl groups of TBP. The hydrochloric acid peak in the TBP complex shifts upfield when the amount of the acid (or x value) increases in the complex. The NMR spectra of the TBP-nitric acid complexes is similar to that of TBP-hydrochloric acid complexes. Figure 2a shows the proton peaks of the TBP(HNO$_3$)$_{0.7}$(H$_2$O)$_{0.7}$ complex. Rapid exchange of H$_2$O and HNO$_3$ in the complex apparently takes place resulting in a single proton resonance peak at about 11.8 ppm. Formation of TBP-acid complex is not limited to hydrophilic inorganic acids. Organic acids can also form hydrogen bonded complex with TBP as illustrated by the NMR spectra of a TBP-benzoic acid complex given in Figure 3. Figure 3a shows the NMR spectrum of benzoic acid alone and Figure 3b shows the spectrum of a TBP(benzoic acid)$_{0.5}$ complex in CDC$_3$. The shift of the carboxylic acid proton peak from the free benzoic acid (12.8 ppm) to the bonded acid (11.8 ppm) is obvious. Peaks at 8.1, 7.6 and 7.5 ppm in Figure 2a are protons from the benzene ring.

Understanding the solvation effect of supercritical CO$_2$ on the TBP-acid complexes is important for evaluating the behavior of the complex in the fluid phase. Unfortunately, the corrosive nature of the complex and the lack of a safe high-pressure NMR device in our lab prevented us from performing NMR studies of the TBP-acid complexes in supercritical CO$_2$. We chose to use chloroform (CDCl$_3$) to evaluate the salvation effect because chloroform has a small dielectric constant at room temperature ($\varepsilon = 4.8$ at 20 °C). Figure 1b shows that in the
presence of CDCl₃, a new peak at 7.9 ppm appears that is close to the NMR peak of free hydrochloric acid. An anti-solvent effect of chloroform probably causes a portion of the hydrochloric acid in the complex to precipitate and forming small droplets in the solvent. The bonded hydrochloric acid in TBP shifts upfield to about 10.3 ppm. Formation of small acid droplets in CDCl₃ was obvious because the solution turned cloudy after addition of the TBP complex to the solvent. The cloud formation was also observed when the TBP-hydrochloric acid complex was added to supercritical CO₂ using a high-pressure view-cell with quartz windows. Similar cloud formation was observed when a TBP(HNO₃)₀.₇(H₂O)₀.₇ complex was added to supercritical CO₂. When the TBP-nitric acid complex was dissolved in CDCl₃, a free nitric acid peak appeared at 6.5 ppm and the bonded nitric acid peak shifted to 12.5 ppm as indicated by the NMR spectrum given in Figure 2b.

Figure 7. Proton NMR spectra of TBP(HCl)₀.₈(H₂O)₂.₈ with D₂O insert (top) and in CDCl₃ (bottom)
Figure 8. Proton NMR spectra of TBP(HNO₃)₀.7(H₂O)₀.7 with D₂O insert (top) and in CDCl₃ (bottom)
The solubilities of some TBP-acid complexes in supercritical CO₂ were measured at 40 °C by visual observation of phase behavior under different pressures using a view cell with quartz windows. Solubility data of TBP and benzoic acid are known in the literature. TBP is highly soluble in supercritical CO₂. According to Joung et al., TBP becomes miscible with supercritical CO₂ above certain pressure at a given temperature. For example, at 50 °C (323.15 K) TBP and CO₂ form one phase at pressures above 110 atm. Nitric acid and hydrochloric acid alone are not soluble in supercritical CO₂ and benzoic acid has a limited solubility in CO₂ (Table 2). When benzoic acid is bonded to TBP, the solubility of the complex is significantly enhanced. For example, the TBP(benzoic acid)₀.₅ complex has a solubility of 1.3 mole% at 40 °C and 114 atm which is about an order of magnitude higher than the free acid alone in supercritical CO₂ under similar conditions. The solubilities of TBP and TBP(HCl)₀.₈(H₂O)₂.₃ and TBP(HNO₃)₀.₇(H₂O)₀.₇ are in the range of 1.0-1.7 mole% in supercritical CO₂ at 40 °C and around 110 atm.
Table 3. Solubilities of some TBP-acid complexes in supercritical CO₂

<table>
<thead>
<tr>
<th>Solute</th>
<th>Temp (°C)</th>
<th>P (atm)</th>
<th>Solubility (mole %)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzoic acid</td>
<td>45</td>
<td>100</td>
<td>0.026</td>
<td>13</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>35</td>
<td>118</td>
<td>0.13</td>
<td>1</td>
</tr>
<tr>
<td>TBP(benzoic acid)₀.₅</td>
<td>40</td>
<td>114</td>
<td>1.3</td>
<td>this study</td>
</tr>
<tr>
<td>TBP(HNO₃)₀.₇(H₂O)₀.₇</td>
<td>40</td>
<td>110</td>
<td>1.7</td>
<td>this study</td>
</tr>
<tr>
<td>TBP(HCl)₀.₈(H₂O)₂.₈</td>
<td>40</td>
<td>116</td>
<td>1.0</td>
<td>this study</td>
</tr>
</tbody>
</table>

* Standard deviations of solubility measurements for this study ~10%

The Lewis acid-base complex formation method described in this paper allows normally insoluble or slightly soluble acids to be dissolved in supercritical CO₂. This method is simple and can introduce a variety of acids in supercritical CO₂ for chemical reactions or separations. The method is not limited to TBP, other commercially available Lewis bases that are CO₂ soluble may also be used as carriers for introducing acids in supercritical CO₂. In principle, this method could also be used to introduce bases in supercritical CO₂ using a CO₂-philic Lewis acid. The Lewis acid-base complex formation concept can also be applied to supercritical CO₂ extraction of acids from aqueous solutions using TBP or other CO₂ soluble Lewis base as a carrier. This simple complex formation concept may have a wide range of applications and research to explore potential applications of this method in supercritical fluid processes is currently in progress.

V. Characterization of a TBP-Nitric Acid Complex for Dissolution of Uranium Dioxide in Supercritical CO₂

The Lewis acid-base complex formation method of dissolving acids particularly nitric acid in supercritical CO₂ is significant because it suggests a possibility of using this CO₂-soluble complex for dissolution of uranium dioxide directly in CO₂. In the conventional Purex (Plutonium Uranium Extraction) process, aqueous nitric acid (3-6 M) is used to dissolve and oxidize UO₂ in the spent fuel to uranyl ions (UO₂)²⁺. The acid solution is then extracted with TBP in an organic solvent such as dodecane, to remove uranium as UO₂(NO₃)₂·2TBP into the organic phase. Direct dissolution of solid UO₂ in SF-CO₂ with a TBP-nitric acid complex obviously has an advantage over the conventional Purex process because it would combine dissolution and extraction steps into one with a minimum waste generation. The chemical nature of the TBP-nitric acid complex and the mechanisms of UO₂ dissolution in SF-CO₂ with the TBP-nitric acid solution are not well known. The TBP-nitric acid complex is prepared by shaking TBP with a concentrated nitric acid solution. Because water is present in the nitric acid solution, the complex is expected to have a general formula of TBP(HNO₃)ₓ(H₂O)ᵧ, where x and y can vary depending on the relative amounts of TBP and nitric acid used in the preparation.

The solubility of water in pure TBP at room temperature is about 64 grams per liter of the solution that is close to a 1:1 mole ratio of TBP/H₂O. In the TBP/H₂O binary system, water is most likely bound to TBP through hydrogen bonding with phosphoryl oxygen forming a 1:1 complex. The bonding between TBP and H₂O in the presence of HNO₃ is unknown. Recent
molecular dynamics investigations suggest that hydronium ions or hydrogen from HNO₃ or H₂O are bonded to the oxygen of the P=O bond in TBP. Knowledge on the equilibrium compositions of the TBP(HNO₃)ₓ(H₂O)ₙ complex prepared by different proportions of the initial TBP and nitric acid is essential for understanding the nature and mechanisms of UO₂ dissolution in SF CO₂. In this section, our initial results of characterizing the TBP(HNO₃)ₓ(H₂O)ₙ complex using several different methods including Karl-Fischer method for water determination, conventional acid-base titration for measurement of HNO₃, nuclear magnetic resonance (NMR) spectroscopy to evaluate chemical environments of protons, and visual observation of phase behavior of the complex in SF-CO₂.

TBP was purchased from Avocado (ordered through Alfa Aesar, Ward Hill, MA). Nitric acid (69.5 % w/w) was obtained from Fisher Chemical (Fair Lawn, NJ), and was diluted to 15.5 M by deionized water. The TBP(HNO₃)ₓ(H₂O)ₙ complex was prepared by mixing 98% TBP with 15.5 M nitric acid at a chosen ratio in a glass tube with a stopper. The mixture of TBP and nitric acid was manually shaken vigorously for 4 minutes, followed by centrifuging for one hour. After phase separation, portions of the TBP phase and the aqueous phase were removed with pipettes for characterization experiments. The concentration of H₂O in the TBP phase was measured by Karl-Fischer titration using an Aquacounter AQ-7 instrument (Hiranuma, Japan). The concentration of HNO₃ in the TBP phase was measured with an automatic titrator (COM-450, Hiranuma, Japan) with 0.1 M NaOH solution after adding an excess amount of deionized water to the organic phase. A typical procedure is by shaking 1 mL of the TBP phase with 50 mL of water. After phase separation, the amount of nitric acid in the aqueous phase was determined by NaOH titration. A 500 MHz NMR spectrometer (BRUKER Advance 500) was used for proton NMR measurements. Phase behavior was studied using a high-pressure view-cell system and a video camera.

The amount of HNO₃ in the complex was evaluated by the acid-base titration method described in the previous paragraph. When the molar ratio of HNO₃/TBP in the organic phase is plotted against the molar ratio of HNO₃/H₂O in the equilibrated aqueous phase, the experimental data appear to show two regions with a breaking point around unity for the HN0₃/TBP ratio (Figure 10). The data seem to suggest that there are two types of the TBP(HNO₃)ₓ(H₂O)ₙ complex. The type I complex would incorporate HNO₃ rapidly into the TBP phase until a 1:1 ratio of HNO₃/TBP is reached. Beyond that point there is another region where incorporation of HNO₃ into TBP becomes slow. According to Figure 10, more than 2 molecules of HNO₃ can be associated with each TBP molecule in the complex if the organic phase is equilibrated with a concentrated nitric acid. TBP is a highly CO₂-soluble Lewis base. Inorganic acids such as nitric acid which are usually insoluble in CO₂ can be made soluble by complexation with a CO₂-soluble Lewis base such as TBP. This Lewis acid-base complex approach may provide a method of dispersing various CO₂ insoluble acids in supercritical CO₂ phase for chemical reactions.

The amount of water in the TBP(HNO₃)ₓ(H₂O)ₙ complex determined by Karl-Fischer method also shows two distinct regions. When the molar ratio of HNO₃/H₂O in the TBP phase is plotted against the molar ratio of HNO₃/H₂O in the equilibrated aqueous phase, it clearly shows two different types of the TBP(HNO₃)ₓ(H₂O)ₙ complex (Figure 11). In region I, the ratio of HNO₃/H₂O in the TBP phase tends to increase with increasing HNO₃/H₂O ratio in the aqueous phase. In region II, the ratio of HNO₃/H₂O in the TBP phase maintains a constant value of about 3 with increasing HNO₃/H₂O ratio in the equilibrated aqueous phase. The ratio of HNO₃/TBP in the organic phase continues to increase with increasing HNO₃/H₂O ratio in the aqueous phase as
shown in Figure 10, but the ratio of HNO$_3$/H$_2$O in the organic phase remains a constant. It
appears that for the type II complex, the nitric acid incorporated into the TBP phase is in a form
with a general formula of 3HNO$_3$·H$_2$O.

The proton NMR spectra of the TBP(HNO$_3$)$_x$(H$_2$O)$_y$ system in supercritical CO$_2$ were
discussed in the previous section. Formation of small nitric acid droplets due to an anti-solvent
effect of supercritical CO$_2$ was observed when the TBP(HNO$_3$)$_{0.7}$(H$_2$O)$_{0.7}$ complex was dissolved
in the fluid phase. The acid droplets probably started with very small particles and aggregated to
certain sizes that would make the solution cloudy. This acid droplets dispersed in the
supercritical CO$_2$ phase may be effective for oxidation of solid UO$_2$ to the uranyl ions (UO$_2$)$_{2+}$
that is followed by the formation of the CO$_2$-soluble UO$_2$(NO$_3$)$_2$·(TBP)$_2$ complex. The solubility
of in supercritical CO$_2$ is very high, reaching about 0.45 mol L$^{-1}$ at 40 °C and 150 atm.

The phase behavior of a TBP(HNO$_3$)$_x$(H$_2$O)$_y$ complex in supercritical CO$_2$ was also
evaluated by visual observation of the solution using a high-pressure view-cell. Figure 12 shows
the phase boundaries of the TBP(HNO$_3$)$_{1.8}$(H$_2$O)$_{0.6}$ complex in supercritical CO$_2$ at three
different temperatures with respect to pressure and mole fraction of the solute. The isothermal
phase boundaries given in Figure 8 represent the transition pressures from a two-phase region
into a single phase solution for the complex with mole fractions greater than 10$^{-4}$. At each
temperature investigated there exists a maximum transition temperature above which the
complex and CO$_2$ are miscible. For example, at 323.15 K the complex becomes miscible with
SF-CO$_2$ at 14 MPa with any mole fractions. This implies that a large amount of the complex can
be dissolved in SF-CO$_2$ above this specific pressure for the given temperature. The maximum
phase transition temperature for the complex increases with temperature of the system varying
from 11 MPa at 313.15 K to 17 MPa at 333.15 K.

![Figure 10](image-url)

**Figure 10.** A plot of $[\text{HNO}_3]/[\text{TBP}]$ ratio in the TBP phase against $[\text{HNO}_3]/[\text{H}_2\text{O}]$ ratio
in the equilibrated aqueous phase.
Figure 11. Molecular ratio of $[\text{HNO}_3]/[\text{H}_2\text{O}]$ in the TBP phase versus that in the equilibrated aqueous phase.

Figure 12. Phase diagram of TBP($\text{HNO}_3)_{1.8}(\text{H}_2\text{O})_{0.6}$ in supercritical CO$_2$. 
VI. Dissolution of Uranium Dioxide in Supercritical CO₂

Direct dissolution of solid UO₂ in supercritical CO₂ is difficult because uranium at +4 oxidation state does not form stable complexes with commonly known ligands. An oxidation step is needed to convert uranium from +4 to +6 oxidation state to make it extractable in supercritical CO₂. Recent reports show that TBP forms a complex with nitric acid which is soluble in supercritical CO₂ and is capable of dissolving lanthanide oxides and uranium oxides directly (8). The complex is prepared by mixing TBP with a concentrated nitric acid solution. Nitric acid dissolves in the TBP phase forming a complex of the general formula TBP(HNO₃)ₓ(H₂O)ᵧ that is separated from the remaining aqueous phase. The TBP-nitric acid complex is soluble in supercritical CO₂ and it is capable of dissolving solid uranium dioxide directly. The UO₂ dissolution process probably involves oxidation of the tetravalent uranium in UO₂ to the hexavalent uranyl followed by formation of UO₂(NO₃)₂·2TBP which is known to have a high solubility in SF-CO₂.

The solubilities of (UO₂)(NO₃)₂·2TBP in supercritical CO₂ in the temperature range 40 °C to 60 °C and pressure range 100 to 200 atm were measured using a spectroscopic method. The solubility of this important uranyl complex in supercritical CO₂ is about 0.4 mol/L at 40 °C and 200 atm. This uranium concentration is similar to that used in the PUREX process. In comparison with UO₂(NO₃)₂·2TBP, the solubility of UO₂(TTA)₂·TBP in supercritical CO₂ is about an order of magnitude lower. These information indicates that uranium and transuranics in solid materials can be extracted directly by supercritical CO₂ containing a TBP-nitric acid complex.

![Figure 13. Dissolution of UO₂ and UO₃ in supercritical CO₂ using TBP(HNO₃)₀.₇(H₂O)₀.₇ as an extractant at 60 °C and 150 atm, flow rate = 0.4 mL/min](image-url)
Dissolution of UO₂ by a TBP-nitric acid complex depends on the stoichiometry of the complex and the density of the supercritical fluid phase. For example, using a supercritical CO₂ stream containing the TBP(HNO₃)₀.₇(H₂O)₀.₇ complex that flows through a UO₂ powder with a flow rate of 0.4 mL/min, the amount of UO₂ dissolves in the supercritical CO₂ stream is shown in Figure 1. The supercritical CO₂ solution was produced by bubbling liquid CO₂ through a cell containing the TBP(HNO₃)₀.₇(H₂O)₀.₇ complex at room temperature (around 23 °C). The dissolution of UO₂ using the TBP(HNO₃)₁.₈(H₂O)₀.₆ complex in supercritical CO₂ is more rapid because of a higher nitric acid concentration provided by the complex. The alkali metals, the alkaline earth metals, and a number of transition metals can not be extracted by the TBP-nitric acid complex in supercritical CO₂. Sonification can enhance the dissolution rate of tightly packed UO₂ powders significantly probably by increasing the transport of UO₂(NO₃)₂(TBP)₂ from the solid surface to the supercritical fluid phase. Dissolution of UO₂ by a TBP-nitric acid complex (e.g. TBP(HNO₃)₀.₇(H₂O)₀.₇ or TBP(HNO₃)₁.₈(H₂O)₀.₆) in supercritical CO₂ is more efficient than the dissolution of UO₂. This can be attributed to the fact that the uranium in UO₃ is already in the +6 oxidation state, thus no oxidation is required in the formation of the uranyl complex UO₂(NO₃)₂(TBP)₂.

In the conventional Purex (Plutonium Uranium Extraction) process, aqueous nitric acid (3-6 M) is first used to dissolve and oxidize UO₂ in the spent fuel to uranyl ions (UO₂)³⁺. The acid solution is then extracted with TBP in dodecane to remove the uranium as UO₂(NO₃)₂•2TBP into the organic phase. The SF-CO₂ dissolution of UO₂ with a TBP-nitric acid complex has advantages over the conventional Purex process since it combines dissolution and extraction into one step with minimum waste generation. This green SF process that requires no aqueous solution and organic solvent may have potential applications for processing spent nuclear fuel, decontamination of UO₂ contaminated wastes, and even for processing of rare earth ores. TBP-nitric acid complex obviously has an advantage over the conventional Purex process because it would combine dissolution and extraction steps into one with a minimum waste generation. Demonstration of this Super-DIREX process (supercritical fluid direct extraction process) is currently underway in Japan involving Mitsubichi Heavy Industries, Japan Nuclear Cycle Corporation, and Nagoya University. The project is aimed at extracting uranium and plutonium from the mixed oxide fuel as well as the irradiated nuclear fuel using a TBP-nitric acid complex in supercritical CO₂.
VII. Appendix – Reprints of the Publications Derived from the Project

See Attached file
An FT-IR Study of Crown Ether–Water Complexation in Supercritical CO2

Anne Rustenholtz,* John L. Fulton, and Chien M. Wai**

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In the presence of 18-crown-6, D2O forms a 1:1 complex with the macrocyclic molecule in supercritical fluid CO2 with two different configurations. The D2O molecule can be bonded to two oxygen atoms of the crown cavity in a bridged configuration that is characterized by a broad peak at 2590 cm⁻¹. The D2O molecule can also form one hydrogen bond with an oxygen atom of the crown cavity that can be characterized by two peaks at 2679 and 2733 cm⁻¹, with the former assigned to the hydrogen-bonded O–D stretching and the latter the unbonded O–D stretching. The equilibrium constants of the two configurations in supercritical CO2 have been calculated. The enthalpy of formation is −12 ± 2 kJ mol⁻¹ for the single-hydrogen-bond complex and −38 ± 3 kJ mol⁻¹ for the bridged configuration complex. At high 18-crown-6 to D2O ratios, the formation of another complex in supercritical CO2 that involves one D2O molecule hydrogen bonded to two 18-crown-6 molecules becomes possible.

Introduction

Supercritical fluids have unique properties that make them highly attractive for extraction of metal ions from liquid and solid materials. Carbon dioxide is most widely used for supercritical fluid applications because of a number of advantages including (i) low toxicity, (ii) environmentally benignity, (iii) low cost, (iv) moderate critical constants (Tc = 31 °C and Pc = 73.7 bar), and (v) tunable solvation strength that varies with density. Selective extraction of metal species using a nonpolar solvent such as CO2 requires special chelating agents that should possess ion recognition ability and be soluble in supercritical fluid carbon dioxide (SF-CO2). Crown ethers have been extensively used for extraction of alkali-metal and alkaline-earth-metal cations from aqueous solutions into organic solvents. The relatively high solubility of crown ethers in liquid and supercritical CO2 and their selectivity for the alkali-metal and the alkaline-earth-metal ions make them attractive for environmental applications such as CO2-based nuclear waste management technology that would result in minimum liquid waste generation.

For the extraction of metal ions from aqueous solutions using ligands dissolved in SF-CO2, the fluid phase will be saturated with water. Thus, water interaction with the ligand in the fluid phase plays an integral role in the extraction process. It has been reported that the extraction efficiency of alkali-metal ions in conventional solvent processes depends on the solubility of water in the organic phase using macrocyclic polyethers as a complexing agent. With crown ethers, both computational simulation and spectroscopic studies show that, in organic solvents, the water can bond to a macrocyclic host molecule by two different types of hydrogen bonding. The first type is composed of a single hydrogen bond between one hydrogen atom of a water molecule and one oxygen atom of the crown cavity. In this case, the water molecule is mostly located outside the cavity. The second type occurs inside the cavity and is composed of a water molecule bridging between two different oxygen atoms of the crown cavity.

FT-IR is a sensitive and qualitative technique that has been used during the past few years to study hydrogen bonding in different solvents. For example, Fulton et al. used this technique to explore hydrogen bonding of methanol dissolved in supercritical carbon dioxide and found that a weak interaction between carbon dioxide and methanol significantly reduced the amount of methanol–methanol hydrogen bonding. Johnston et al. used it to understand the solvent effect on hydrogen bonding in supercritical fluids. They were able to determine, with a good accuracy, the equilibrium constants and other thermodynamics data for the hydrogen bond between methanol and triethylamine. The FT-IR technique has also been used by Meyer et al. to determine how water is bonded to crown ethers in carbon tetrachloride. These authors assigned vibrational bands to free water and to two different kinds of hydrogen bonds mentioned above. In this paper we examine the interactions of water and 18-crown-6 in liquid and supercritical CO2 for the purpose of establishing a basis for using this green solvent in extraction processes utilizing crown ethers as extractants.

Experimental Section

A specially designed high-pressure IR cell capable of operation to 500 bar was used for this study. The 9.2 mL internal volume cell is built in stainless steel block. The infrared beam is focused along two conical holes and passes through two small diamond windows providing a path length of 100 mm. The cell has one observation window (sapphire) sealed with a gold-plated metal V-ring seal, which allows visual determination of the number of phases present inside the cell. For quantitative analysis it is essential to avoid formation of a second aqueous phase on the beam path windows, which would interfere with data collection. A Teflon-coated magnetic stirring bar was introduced into the cell, allowing stirring of the solution while the cell was placed inside an FT-IR spectrometer.
A syringe pump (ISCO, model 100DX) was used to supply liquid CO₂ to the cell that was preloaded with the starting chemicals. The pressure was measured using an electronic transducer (Precise Sensor Inc., model 4451-10) with a ±1 bar accuracy. The cell was placed on a lightweight ceramic stand, thermally isolated with an insulation coat, and heated using four electric cartridge heaters. The temperature was controlled with a controller (Watlow) having a ±1 °C accuracy. A Bruker IFS 66v FT-IR spectrometer with a mercury-cadmium-telluride (MCT) detector (Kolmar Technologies) was used to acquire all IR spectra. To obtain a good signal-to-noise ratio, the acquisition time was set at 5 min (corresponding to approximately 2350 scans), the scanner velocity was 80 kHz set for 4 cm⁻¹ resolution. A background spectrum of the empty cell (with diamond windows) was subtracted from each sample spectrum. Deuterated water (D₂O) was used rather than H₂O to avoid overlapping of water and intense CO₂ absorption bands between 3500 and 3800 cm⁻¹. The existence of weak 18-crown-6 bands between 2760 and 2680 cm⁻¹ (C-H stretch) which overlap with the D₂O signal required a spectrum of the pure crown ether in liquid CO₂, to be subtracted from the sample spectrum for background correction.

D₂O (100% D, 99.96% pure), 18-crown-6 (99.5% pure), dicyclohexano-18-crown-6 (98% pure), methanol-d (99.5+ atom % D), and carbon tetrachloride (99.9% pure) were purchased from Aldrich Chemical Co. and used without further purification. Carbon dioxide was obtained as supercritical fluid chromatography (SFC) grade (purity >99.99%) from Scott Specialty Gases Inc. The pure CO₂ density varies in this study between 0.66 and 1.04 g mL⁻¹ by tuning the temperature between 25 and 70 °C and the pressure between 200 and 400 bar. The pure CO₂ density was determined using a reported table from the NIST (National Institute of Standards and Technology) Chemistry WebBook.

To avoid water contamination from the atmosphere, the cell was purged with nitrogen and the chemicals were handled and introduced using a glovebox purged with nitrogen. The solutions were stirred for 20–30 min to reach equilibrium after each density or concentration change. Longer equilibrium times were briefly explored, but no significant change in the IR spectra was observed. Curve fitting and other spectrum analysis and corrections have been performed with standard spectral software (OPUS, Bruker Optik).

**Results and Discussion**

To study the nature of crown–water hydrogen bonding in liquid and SF-CO₂, we examined FTIR spectra of a series of mixtures with 18-crown-6 concentrations varied from 0 to 0.25 mol L⁻¹ and the total D₂O concentration fixed at 49 mmol L⁻¹. The D₂O concentration was below the known solubility of water in pure CO₂ under our experimental conditions. This fact was supported by the observation of a single phase for all the CO₂ experiments conducted in this study.

**Peak Assignment.** FT-IR spectra for different crown ether concentrations (0–0.25 mol L⁻¹) and a fixed D₂O concentration (0.049 mol L⁻¹) are shown in parts a and b of Figure 2 for liquid and SF-CO₂, respectively. Peaks for the free D₂O, i.e., D₂O dissolved in SF-CO₂ without the crown ether (O–D stretching, asymmetric at 2761 cm⁻¹ and symmetric at 2654 cm⁻¹), can be easily discerned, and their positions are in agreement with those reported for D₂O molecules in the vapor (i.e., 2789 and 2666 cm⁻¹ for the D₂O vapor). The shifts of the D₂O vibrational stretchings to lower wavenumbers in SF-CO₂ relative to those of single molecules in the vapor phase reflect the interactions of D₂O molecules with CO₂ in the fluid phase. When 18-crown-6 was added to the CO₂ solution, three other peaks at 2733, 2679, and 2590 cm⁻¹ appeared. According to the order of peak assignment of H₂O-18-crown-6 complex in carbon tetrachloride, the broad peak at 2590 cm⁻¹ should correspond to the symmetrical stretch of the O–D bond involved in the two-hydrogen-bond bridge as illustrated in Figure 1a. The D₂O molecule with one hydrogen bond to the cavity oxygen is expected to have two stretching bands. The sharp O–D band at 2733 cm⁻¹ should be the unbonded O–D stretching marked as 2 in Figure 1b. The bonded O–D stretching band (marked as 1 in Figure 1b) was assigned to the 2679 cm⁻¹ peak, located between the symmetrical and the asymmetrical stretching bands of free water. In the FT-IR spectra of the H₂O-18-crown-6 complex in CCl₄, the bonded O–H stretching band was found at a lower energy than the symmetrical stretch band of free water. We confirmed our assignment of this bonded O–D band by completing two secondary experiments. One experiment was a comparison of the FTIR spectra of 18-crown-6–H₂O and 18-crown-6–D₂O complexes in CCl₄. We confirmed the peak assignment of the former as reported in the literature, and the D₂O isotopic effect altered the peak order of the latter as shown in Figure 2. In another experiment, we confirmed that the order and assignment of the various O–D bands in the 18-crown-6–D₂O complex in SF-CO₂ were the same in both CCl₄ and liquid CO₂.

We also obtained the FT-IR spectra of methanol-d mixed with the crown ether in supercritical CO₂ (Figure 3a). The peaks between 2860 and 3100 cm⁻¹ correspond to the stretching of the C–H bonds belonging to the methanol-d molecule. Due to a different O–D bond energy for methanol-d vs D₂O, the peak maximum of the O–D stretching mode for methanol-d is shifted.

**Figure 1.** Scheme of the three possible bondings between D₂O and 18-crown-6: (a) bridge bonding; (b) single bonding; (c) 1:2 complex in a sandwich configuration.
a) 25°C & 400 bars

![Absorbance vs Wavenumber (cm⁻¹) for 25°C and 400 bars](image1.png)

**Figure 2.** FT-IR spectra of free and bonded D₂O at different 18-crown-6 concentrations (0-0.25 mol L⁻¹) and at one fixed D₂O concentration (0.049 mol L⁻¹) in liquid (a, 25 °C and 400 bar) and supercritical (b, 40 °C and 400 bar) CO₂.

b) 40°C & 400 bars

![Absorbance vs Wavenumber (cm⁻¹) for 40°C and 400 bars](image2.png)

**Figure 2.** FT-IR spectra of free and bonded D₂O at different 18-crown-6 concentrations (0-0.25 mol L⁻¹) and at one fixed D₂O concentration (0.049 mol L⁻¹) in liquid (a, 25 °C and 400 bar) and supercritical (b, 40 °C and 400 bar) CO₂.

<table>
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<tr>
<th>Concentration (M)</th>
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<tbody>
<tr>
<td>0.041 M</td>
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</tr>
<tr>
<td>0.082 M</td>
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</tr>
<tr>
<td>0.123 M</td>
<td></td>
</tr>
<tr>
<td>0.165 M</td>
<td></td>
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<td>0.247 M</td>
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</table>

**Figure 3.** (a) Free methanol-d (0.17 mol L⁻¹) and methanol-d (0.17 mol L⁻¹) complexed to 18-crown-6 (0.02 mol L⁻¹) in CO₂ (40 °C and 200 bar). (b) Free D₂O (49 mmol L⁻¹) and D₂O (49 mmol L⁻¹) complexed to dicyclo-18-crown-6 (0.06 mol L⁻¹) in CO₂ (40 °C and 300 bar). (c) D₂O (respectively 17 and 49 mmol L⁻¹) complexed to 18-crown-6 (respectively at 0.40 mol L⁻¹ (−), 0.041 (− − −), and 0.123 (−) mol L⁻¹) in CO₂ at respectively, 40 °C and 200 bar and 40 °C and 400 bar.

to a higher energy. Nevertheless, both asymmetric and symmetric free O-D stretching peaks (respectively at 2841 and 2701 cm⁻¹) were observed in the spectra shown in Figure 3a. Moreover, only the bonded O-D stretching band (similar to 1 in Figure 1b) appeared at the expected position (i.e., 2609 cm⁻¹). These observations provided further support for our peak assignment.

Recent molecular dynamic simulation studies performed by Wipff et al.²⁰ for 18-crown-6 and water in SF-CO₂ suggest that most of the water molecules were bridge bonded to crown ether in the D₃d conformation. The observation of a singly bonded water to a crown complex in our experiments could be due to the flexibility of the macrocyclic molecule; 18-crown-6 can be in various conformations that may favor a singly or a doubly bonded water molecule. The 18-crown-6 cavity in dicyclohexano-18-crown-6 is forced by its geometry into the D₃d conformation and is supposed to be rigid. The FT-IR spectra of D₂O with and without dicyclohexano-18-crown-6 in SF-CO₂ are shown in Figure 3b. The spectrum shows that the free D₂O stretching bands are observed at 2761 (asymmetric) and 2653 (symmetric) cm⁻¹. For the D₂O with crown solution both single hydrogen bonding (at 2701 (bonded) and 2732 (unbonded) cm⁻¹) and double hydrogen bonding (at 2591 cm⁻¹) with the oxygen atoms of the macrocyclic cavity, similar to that found in 18-crown-6, are observed. The difference between our spectroscopic study and Wipff's molecular dynamic simulation may be due to differences in species concentrations and CO₂ densities used in the simulation study.
TABLE 1: Apparent Molar Absorptivity at Different CO2 Densities

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</table>

* \(e_1\), free D2O asymmetric (2761 cm\(^{-1}\)) stretching band; \(e_2\), free D2O symmetric (2654 cm\(^{-1}\)) stretching band; \(e_3\), doubly bonded D2O to crown band (at 2593 cm\(^{-1}\)); \(e_4\) and \(e_5\), C–H stretch band of 18-crown-6 at 2872 and 2947 cm\(^{-1}\), respectively.

1:2 Complex Formation. When the 18-crown-6 concentration exceeds 0.4 mol L\(^{-1}\) with a lower water concentration (less than 17 mmol L\(^{-1}\)), only one absorption band at 2590 cm\(^{-1}\) is observed (Figure 3c). All the D2O molecules seem to be bridge bonded to the crown ether. This observation may be explained by the formation of a 1:2 complex between D2O and 18-crown-6 as illustrated in Figure 1c. The O–D stretching band for this kind of complex should appear at the same frequency as that of the bridged form of D2O (Figure 1a configuration). Our suggestion of 1:2 complex formation is based on the assumption that, by increasing the crown ether to water ratio in SF-CO2, we do not change the equilibrium between D2O molecules bonded to one oxygen atom (configuration 1b) or to two oxygen atoms (configuration 1a) of the cavity. As the concentration of 18-crown-6 in the system increases, it is conceivable that the singly bonded D2O molecule (configuration 1b) would form a hydrogen bond with another crown molecule via the unbonded O–D, thus leading to the formation of a 1:2 complex. The law of mass action should favor the shifting of equilibrium from a 1:1 complex to a 1:2 complex between water and 18-crown-6 in SF-CO2. Also in Figure 3c, we show, for comparison, spectra of the double bond area of 18-crown-6 (at 0.041 and 0.123 M) and D2O (0.049 M) at 400 bar and 40 °C. Peaks occur at the same position for both the dimer and the monomer forms.

The sandwich form (configuration 1c) is a probable conformation for the 1:2 complex, but other configurations (e.g., from offset to perpendicular) can be envisaged. Formation of 1:2 complexes has been reported for crown ether extraction of metal ions from aqueous solutions where a metal ion can bond to two crown cavities to form a sandwich complex. We are not aware of any previous report regarding a 1:2 complex formation between water and crown molecules. Our experimental data indicate that, with increasing crown to D2O ratios in the SF-CO2 system, the intensities of the single-hydrogen-bond D2O stretching peaks (2735 and 2679 cm\(^{-1}\)) decreases and that of the peak at 2590 cm\(^{-1}\) increases. Although the 1:2 complex forms at high crown to D2O ratios, we cannot distinguish the bridging 1:1 complex (configuration 1a) and the 1:2 complex (configuration 1c) from the FT-IR spectra.

Molar Absorptivity Calculation. A number of experimental parameters (e.g., path length change, radiation of the cell, etc.) can influence molar absorptivity values in addition to pressure and temperature effects in SF-CO2 as reported in the literature.\(^{22}\) Therefore, for quantitative discussion of FT-IR data, molar absorptivity should be evaluated for each SF-CO2 condition.\(^{24}\)

The molar absorptivities for free D2O dissolved in CO2 (Table 1 and Figure 4) were determined by the analysis of FT-IR spectra with pure D2O of known concentrations. The apparent molar absorptivity of D2O, in liquid and supercritical CO2, increases with the fluid density. This behavior is similar to that reported for pyrene and anthracene\(^{21}\) in CO2 solutions. In our system, the molar absorptivity for the asymmetric stretching band of the free D2O at 2761 cm\(^{-1}\) is more than doubled for an increase in CO2 density from 0.66 to 1.04 g mL\(^{-1}\). The molar absorptivities of the C–H stretching vibrations of pure 18-crown-6 dissolved in CO2 at its maximum intensity (2872 cm\(^{-1}\)) and at 2947 cm\(^{-1}\) are also given in Figure 4. A 20% decrease in molar absorptivity is observed for both wavenumbers when the CO2 density varies from 0.65 to 1.0 g mL\(^{-1}\). Because of the stability of those C–H stretches, this decrease might reflect changes in molecular absorptivities due to experimental parameters and needs to be considered to determine true molecular absorptivities. Molar absorptivity changes for free D2O stretching vibrations might be caused by a change in solute–solvent interaction and in solvent refractive index.

The molar absorptivity of the bridging 1:1 complex was determined in the following way. We assumed that the molar absorptivities of the 1:1 bridge complex and the 1:2 complex were similar. Thus, the molar absorptivity of the bridged 1:1 complex could be obtained from the region with high 18-crown-6 to D2O ratios in SF-CO2. Its value (Table 1 and Figure 4) at 2593 cm\(^{-1}\) does not seem to be affected by the change in density. However, the weak solubility limit of 18-crown-6 at low CO2 density did not permit this calculation for a density below 0.8 g mL\(^{-1}\).

Equilibrium Constants and Enthalpy Calculations. The formation of a 1:1 complex between 18-crown-6 and D2O in
the total concentration introduced in the cell. The pressure varies from 200 to 400 bar at constant temperature (40 °C). [18C6] = 41 mmol L⁻¹, [D₂O] = 49 mmol L⁻¹.

Density effect on equilibrium constants

\[ \text{Density of CO}_2 \ (\text{g} \text{cm}^{-3}) \]

The molar enthalpy of a hydrogen bond in liquid CO₂ and D₂O is 20 times larger than that in CCl₄. This implies that, in terms of hydrogen bonding, water behaves as nonpolar solvents such as CCl₄ and supercritical CO₂. The hydrogen-bonding process in both liquid solvents and supercritical fluids is exothermic and that the bonded species are more entropically favored.

The influence of density (increase in pressure from 200 to 400 bar) at a constant temperature (40 °C) on the two equilibrium constants \( K_a \) and \( K_b \) is shown in Figure 5. An increase in density causes a decrease in the \( K_a \) and \( K_b \) values.

The molar enthalpy of a hydrogen bond (\( \Delta H \)) can be determined from the equilibrium constant at constant pressure by eq 4 from well-known thermodynamic relations (eq 3), where \( T \) is the absolute temperature in (K) and \( R \) the ideal gas constant.

\[ \frac{\Delta (\ln K_i)}{\Delta (1/T)} \bigg|_p = -\frac{\Delta H_i}{R} \]

Using a linear regression on the plot of ln \( K \) versus 1/\( T \) for both isomers (i.e., single bond (A) and double bond (B)) between D₂O (49 mmol L⁻¹ total concentration in CO₂) and the 18-crown-6 (83 mmol L⁻¹ total concentration in CO₂) versus temperature (°C), density, the \( \Delta H \) (for a single hydrogen bond, configuration 1b) was found to be \(-12 \pm 2 \text{kJ mol}^{-1}\) and \( \Delta H_b \) (for bridge bonding, configuration 1a) to be \(-38 \pm 3 \text{kJ mol}^{-1}\), both at 200 bar. The complexation process is exothermic as expected for hydrogen bonding, and its value is similar to the literature values for hydrogen-bonding processes in liquid water.

**Isomeric Ratio of the Crown-Water Complex.** The relative concentrations of the singly bonded and the doubly bonded water-crown complexes change with temperature as shown in Figure 7. At a low crown to water mole ratio (about 0.8), the trend is similar for both isomers. When the temperature is increased from 25 to 50 °C at 200 bar, the concentrations of both the singly bonded and the doubly bonded complexes tend to decrease (Figure 7). The decrease for the doubly bonded complex is perhaps slightly faster than the decrease for the singly bonded complex. This can be explained by an entropy effect, i.e., at higher temperatures the more disordered form should be favored.
hydrogen bonds reported in liquid solvents. Molecules becomes possible.

Conclusions

FT-IR is a sensitive technique for studying crown ether and water interactions in SF-CO2. The O–D stretching vibrations for D2O dissolved in SF-CO2 show slight shifts to lower wavenumbers relative to those found for D2O in its vapor phase, indicating interactions (salvation) of CO2 with D2O molecules in the supercritical fluid phase. In the presence of 18-crown-6, D2O forms a 1:1 complex with the macrocyclic molecule with two different configurations. The D2O molecule can form one hydrogen bond with an oxygen atom of the crown cavity, or it can be bonded to two oxygen atoms of the cavity in a bridged configuration. The equilibrium constant of the single-hydrogen-bond configuration is slightly greater than the two-hydrogen-bond configuration, and both equilibrium constants decrease with increasing temperature. The enthalpy of the complex formation is $-12 \pm 2$ kJ mol$^{-1}$ for the former and $-38 \pm 3$ kJ mol$^{-1}$ for the latter. These values are within the range of hydrogen bonds reported in liquid solvents. At high 18-crown-6 to D2O ratios, formation of a 1:2 complex in SF-CO2 that involves one D2O molecule hydrogen bonded to two crown ether molecules becomes possible.

Acknowledgment. This work was supported by the DOE Office of Environment Management, EMSP Program (Grant No. DE-FG07-98ER 14913). Work by J.L.F. was supported by the Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract DE-AC06-76RLO 1830 with Pacific Northwest National Laboratory.

References and Notes

Hydrophilic acids can be dissolved in supercritical CO₂ by a Lewis acid-base complex formation method using a CO₂philic base tri-n-butylphosphate as a carrier.

Supercritical fluid processing has been a burgeoning area of research in recent years for both theoretical and practical considerations. Carbon dioxide (CO₂) is the most widely used gas for supercritical fluid applications because of its moderate critical constants, nonflammable nature and environmental acceptability. However, since CO₂ is non-polar and has a low dielectric constant, supercritical CO₂ (SC-CO₂) processing is limited by its poor ability to dissolve hydrophilic species. Several strategies have been developed in the past to make SC-CO₂ more “solute-philic” including modifying CO₂ with polar solvents, utilizing water-in-CO₂ microemulsions, and complex formation approaches. Recently, dissolution of hydrophilic metal species in SC-CO₂ has gained increasing attention because of potential applications in nuclear waste treatment, environmental remediation, semiconductor devices manufacturing, and chemical catalysis. The in situ chelation method for dissolving metal species in SC-CO₂ developed by our research group in the early 1990s is widely used today for chemical and environmental studies. Several previous reports have demonstrated that the solubility of metal chelates in SC-CO₂ can be significantly enhanced using CO₂-philic ligands such as fluorinated chelating agents and organophosphorous ligands. Among these reagents, tri-n-butylphosphate (TBP) is particularly interesting because it is a CO₂-philic Lewis base and is capable of forming stable coordination compounds with Lewis acids through the electron donating P=O group. The Lewis acid-base complex formation mechanism provides a simple method of dissolving hydrophilic acids in SC-CO₂ using TBP as a carrier. This technique may have a wide range of applications in developing CO₂-based processes because acids are often needed for chemical reactions and separations. The general Lewis acid-base concept of introducing hydrophilic species in SC-CO₂ should not be limited to TBP. In principle, other CO₂ soluble Lewis bases and Lewis acids could also be used as carriers for dissolution of acid or base counterparts in SC-CO₂. This communication presents some examples of Lewis acid-base complexes using TBP as a carrier and their solubilities in SC-CO₂.

The complexes used in this study were prepared by shaking 5 mL of TBP (Aldrich, Milwaukee, M) with a certain amount of an acid in a capped vial for one hour. Concentrated HNO₃ (15.5 M, Fisher, Fair Lawn, NJ), HCl (12.3 M, Fisher), and benzoic acid (Fisher) were used as received for this study. After shaking, the mixture was centrifuged for one hour and the TBP phase was removed for characterization. The acid content in the TBP phase was determined by diluting 1 mL of the TBP phase with 40 mL of water followed by NaOH (0.1 M) titration of the acid in the aqueous phase. The water content of the TBP phase was determined by Karl-Fischer titration. The TBP-acid complex has a general composition of TBP (Acid)ₓ (H₂O)ᵧ with x and y depending on the relative amount of TBP and the acid used in the preparation. Examples of TBP-HNO₃ and TBP-HCl complexes are given in Table 1. The TBP-benzoic acid complex was prepared by dissolving a certain amount of solid benzoic acid in TBP directly. Because benzoic acid does not contain water the complex has a formula of TBP (Acid)ₓ.

### Table 1. Compositions of some TBP-acid complexes prepared for this study

<table>
<thead>
<tr>
<th>Initial TBP/acid mixture</th>
<th>Composition of TBP-acid complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mL TBP + 0.82 mL HNO₃ (15.5 M)</td>
<td>TBP(HNO₃)ₓ(H₂O)ᵧ</td>
</tr>
<tr>
<td>5 mL TBP + 1.3 mL HNO₃ (15.5 M)</td>
<td>TBP(HNO₃)ₓ(H₂O)ᵧ</td>
</tr>
<tr>
<td>5 mL TBP + 1.5 mL HCl (12.3 M)</td>
<td>TBP(HCl)ₓ(H₂O)ᵧ</td>
</tr>
<tr>
<td>5 mL TBP + 2 g benzoic acid</td>
<td>TBP(benzoic acid)ₓ</td>
</tr>
</tbody>
</table>

Proton NMR spectra of a typical TBP-HClₓ(H₂O)ᵧ complex (a) and a TBP-HNO₃ₓ complex (b) are given in Fig. 1. The spectra were taken using a 300 MHz (Bruker) spectrometer at room temperature. In the NMR measurement of pure complexes, deuterated water was placed in an insert and fitted into an NMR tube containing a TBP-acid complex. The purpose of the D₂O
insert was to lock the NMR. A trace amount of HDO present in the deuterated water allows calibration of the instrument. TBP is known to form a 1:1 complex with H$_2$O and the TBP-H$_2$O complex has a single resonance peak at about 3.9 ppm. The proton NMR spectrum of the TBP(HCl)$_{0.8}$(H$_2$O)$_{2,8}$ complex shows a single peak around 8.5 ppm indicating the presence of H$_2$O and HCl in the complex undergo rapid exchange (Fig. 1(a), top). The other 4 peaks below 4 ppm are the protons from the butyl groups of TBP. The HCl peak in the TBP complex shifts downfield when the amount of the acid (or x value) increases in the complex. The NMR spectra of the TBP-HNO$_3$ complexes are similar to that of TBP-HCl complexes. Fig. 1(b) shows the proton peaks of the TBP(HNO$_3$)$_{0.7}$(H$_2$O)$_{2,7}$ complex. Rapid exchange of H$_2$O and HNO$_3$ in the complex apparently takes place resulting in a single proton resonance peak at about 11.8 ppm. Formation of TBP-acid complex is not limited to hydrophilic inorganic acids. Organic acids can also form hydrogen bonded complex with TBP as illustrated by the NMR spectra of a TBP-benzoic acid complex given in Fig. 2. Fig. 2, (top) shows the NMR spectrum of benzoic acid in CCl$_4$ with D$_2$O insert and Fig. 2 (bottom) shows the spectrum of a TBP(benzoic acid)$_{0.5}$ complex with D$_2$O insert. The shift of the carboxylic acid proton peak from the free benzoic acid (6.4 ppm) to the bonded acid (11.8 ppm) is obvious. Peaks at 8.1, 7.6 and 7.4 ppm in Fig. 2 are protons from the benzene ring.

![Proton NMR spectra of benzoic acid alone in CCl$_4$ with D$_2$O insert (top) and TBP(benzoic acid)$_{0.5}$ complex with D$_2$O insert (bottom)](image)

Understanding the solvation effect of SC-CO$_2$ on the TBP-acid complexes is important for evaluating the behavior of the complex in the fluid phase. Unfortunately, the corrosive nature of the complex and the lack of a safe high-pressure NMR device in our lab prevented us from performing NMR studies of the TBP-acid complexes in SC-CO$_2$. We chose to use chloroform (CDCl$_3$) to evaluate the salvation effect because chloroform has a small dielectric constant at room temperature ($\varepsilon$ = 4.8 at 20 °C). Fig. 1(a), (bottom) shows that in the presence of CDCl$_3$, a new peak at 7.1 ppm appears that is attributed to the presence of free HCl. An anti-solvent effect of chloroform probably causes a portion of the HCl in the complex to precipitate and forming small droplets in the solvent. The bonded HCl in TBP shifts downfield to about 10.0 ppm. Formation of small acid droplets in CDCl$_3$ was obvious because the solution turned cloudy when the TBP-HCl complex was added to the solvent. The cloud formation was also observed when the TBP-HCl complex was added to SC-CO$_2$ using a high-pressure view-cell with quartz windows. Similar cloud formation was observed when a TBP(HNO$_3$)$_{0.7}$(H$_2$O)$_{2,7}$ complex was added to SC-CO$_2$. When the TBP-HNO$_3$ complex was dissolved in CDC$_3$, a free HNO$_3$ peak appeared at 6.5 ppm and the bonded HNO$_3$ peak shifted to 12.5 ppm as indicated by the NMR spectrum shown in Fig. 1(b), (bottom). The solubilities of some TBP-acid complexes in SC-CO$_2$ were measured at 40 °C by visual observation of phase behavior under different pressures using a view cell with quartz windows. Solubility data of TBP and benzoic acid are known in the literature. TBP is highly soluble in SC-CO$_2$. According to Joung et al., TBP becomes miscible with SC-CO$_2$ above certain pressure at a given temperature. For example, at 50 °C (523.15 K), TBP and CO$_2$ form one phase at pressures above 110 atm. Hydrochloric acid and nitric acid are not soluble in SC-CO$_2$ and benzoic acid has a limited solubility in CO$_2$ (Table 2). When benzoic acid is bonded to TBP, the solubility of the complex is significantly enhanced. For example, the TBP(benzoic acid)$_{0.5}$ complex has a solubility of 2.4 mole% at 40 °C and 120 atm which is about an order of magnitude higher than the free acid alone in SC-CO$_2$ under similar conditions. The solubilities of TBP and TBP(HCl)$_{0.8}$(H$_2$O)$_{2,8}$ and TBP(HNO$_3$)$_{0.7}$(H$_2$O)$_{2,7}$ are in the range of 1.0-1.7 mole% in SC-CO$_2$ at 40 °C and around 115 atm.

The Lewis acid-base complex formation method described in this paper allows normally insoluble or slightly soluble acids to be dissolved in SC-CO$_2$. This method is simple and can introduce a variety of acids in SC-CO$_2$ for chemical reactions or separations. The method is not limited to TBP, other commercially available Lewis bases that are CO$_2$ soluble may also be used as carriers for introducing acids in SC-CO$_2$. In principle, this method could be used to introduce bases in SC-CO$_2$ using a CO$_2$-philic Lewis acid. The Lewis acid-base complex formation concept may also be applied to SC-CO$_2$ extraction of acids from aqueous solutions using TBP or other CO$_2$ soluble Lewis base as a carrier. Research to explore potential applications of this method in supercritical fluid processes is currently in progress.

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### Notes and references


Nuclear Laundry Using Supercritical Fluid Solutions

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Cobalt and other metals, spiked onto lab coats, can be removed by supercritical fluid carbon dioxide (SC-CO₂) containing mixed chelating agents Cyanex 302 and dithiocarbamate, as well as by a water-in-CO₂ microemulsion. The extraction efficiencies for both methods can exceed 90%. The mixed-ligand approach suggests that effective metal extraction can be developed using two different ligands contributing to the solubility and stability of the resulting metal chelates in SC-CO₂. The water-in-CO₂ microemulsion method does not require chelating agents. This approach significantly reduces the amount of liquid waste generation. Dynamic extraction time, flow rate, temperature of outlet restrictor, and collection solvent must be taken into consideration for the recovery efficiency. The potential of utilizing supercritical fluid solutions for cleaning ⁶⁰Co-contaminated protective coats used by nuclear power plant workers is discussed.

Introduction

Supercritical fluid carbon dioxide (SC-CO₂) has been extensively studied in the past two decades and has come to be recognized as an environmentally friendly solvent for the dissolution of organic compounds that has been traditionally done using organic solvents. In recent years, the studies of supercritical fluid extraction (SFE) techniques for using CO₂ as a solvent to remove metal species from solids have also been reported by various research groups.[1-9] Metal ions do not dissolve in nonpolar SC-CO₂ because of the charge neutralization requirement and weak solute-solvent interactions. Wai and co-workers first reported in the early 1990s that, using an organic chelating agent such as diethylthiocarbamate [(C₂H₅)₂NCS₂⁻, DDC], metal ions could be extracted by SC-CO₂ as dithiocarbamates complexes.² Fluorination of the terminal ethyl groups of metal dithiocarbamate complexes was found to enhance the solubility in SC-CO₂ by 2-3 orders of magnitude.³ This discovery has been one of the key developments in supercritical fluid research. Later, many fluorinated chelating agents including fluorinated β-diketones and fluorinated polymers with various chelating heads were used for dissolution of metal species in SC-CO₂ using this in situ chelation/SFE method.³-⁹ Other types of chelating agents, particularly organophosphorus reagents, such as tri-n-butyl phosphate, bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302), etc., also form CO₂-soluble complexes with various metal species.¹⁰-¹² These ligands and chelating agents have been used to extract transition metals, lanthanides, and actinides from solid samples of different matrices in SC-CO₂. After SFE, depressurizing the supercritical fluid solution results in rapid precipitation of the solutes (metal chelates) from the solvent, leaving decontaminated samples behind. This in situ chelation/SFE method is obviously attractive for removing toxic metals and radioisotopes from contaminated substances.

The radioactive contamination level on protective coats worn by nuclear power plant workers is generally required to be kept below 4 Bq/cm².¹³ Above this level, washing of contaminated coats is often required. The main radioactive isotope in contaminated protective coats is ⁶⁰Co, which emits β (Eₐₓₙ 0.32 MeV) and γ (1.173 and 1.333 MeV) radiations with a half-life of 5.26 years. The contaminated protective coats are commonly washed with water and detergent to remove the radioactive contamination. However, treatment of the wastewater from the conventional nuclear laundry becomes an environmental problem.

More recently, water-in-CO₂ microemulsions have been shown to be an effective medium for transporting metal ions in SC-CO₂.⁵ Relatively high concentrations of metal salts can be dissolved in the water core of the microemulsion and dispersed in the CO₂ phase. The water-in-CO₂ microemulsions are dynamic in nature, and exchange of contents in the water core can take place effectively during collisions. Because of their small size and dynamic nature, these microemulsions show great promise as transporting media for removing metal species from solid materials into SC-CO₂. Using the CO₂ microemulsion to remove metal species from porous solid materials requires only a small amount of water. In comparison with a conventional washing or acid leaching process, which usually requires large quantities of water, the CO₂ microemulsions technique could greatly minimize liquid waste generation. Thus, water-in-CO₂ microemulsions may be regarded as a new solvent for decontamination of radioactive materials. In this paper, we report our recent results regarding SFE of cobalt and other metals from lab coats using in situ chelation/SFE with Cyanex 302 and a dithiocarbamate reagent as extractants. A synergistic effect of the two chelating agents for removing cobalt and other transition metals is described. The results are compared with that obtained using a water-in-CO₂ microemulsion as a medium for removing these metals from fabric matrices.

Experimental Section

Reagents and Materials. Cyanex 302 (Cytec Industries Inc.) and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, Cytec Industries Inc.) were used as supplied (Figure 1). Instrument grade carbon dioxide (Oxarc, Spokane, WA) was used in all experiments. Nitric acid (J. T. Baker) was Ultrace grade ultrapure reagent. Sodium diethyldithiocarbamate [(C₂H₅)₂NCS₂⁻, NaD-

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A commercial liquid detergent (Liqui-Nox) was used for conventional cleaning. Ammonia pyrrolidinedithiocarbamate, [((CH₃)₂NCS]^-·N^+(CH₃)₄, DBDC] and other chemicals, including Sr(NO₃)₂, La(NO₃)₃·6H₂O, and Eu(NO₃)₃·3H₂O salts were obtained from Aldrich Chemical Co. (Milwaukee, WI). Sodium bis(2-ethylhexyl)sulfosuccinate (AOT, Aldrich Chemical Co.) and perfluoropolyether phosphate (PFPE-PO₄) (KDP-4413, Lot No. B86576G-64, DuPont Co.) were used as received. All other reagents and solvents used in this study were of analytical grade. Deionized water (Milli-Q system, Bedford, MA) was used for the preparation of all aqueous solutions. Standard solutions of cobalt chloride and nitrate solutions of Cu, Cd, Pb, and Zn were prepared from atomic absorption spectroscopy standards (EM Science, a Division of EM Industries, Inc., Cherry Hill, NJ).

**Instrumentation.** The apparatus for the SFE experiments (Figure 2) includes the following: a liquid CO₂ tank, a high-pressure syringe pump, an extraction cell, and a collection vial. SFC-grade CO₂ was supplied with a syringe pump (Isco, model 260D, Lincoln, NB). The experiments were performed with a stainless steel extraction vessel (35.3 mL) maintained at a desired temperature by placing it in a thermostatic oven. The flow rate of the extraction fluid was controlled by the Isco pump. At the oven exit, a stainless steel tube (316 SS, 1/16-in. o.d. and 0.030-in. i.d.) with a length of 20 cm was used as the pressure restrictor for the exit CO₂.

A high-pressure view cell (18.8 mL, volume and 5 cm path length) with sapphire windows was used to evaluate the solubility and stability of the water-in-CO₂ microemulsions. A high-pressure fiber-optic cell equipped with a CCD array UV-visible spectrometer was used for in situ spectroscopic measurements. Descriptions of the view cell and fiber-optic system are given in the literature.

**Metal Extraction with Chelating Agents.** A 10-μL sample of a standard solution containing 1000 ppm each of Co, Cd, Cu, Pb, and Zn was spiked on pieces (0.6 × 4 cm²) of fabric cut from a laboratory coat. After evaporation to dryness, the fabric sample was placed on the stainless steel rack in the extraction vessel as shown in Figure 2. The system was pressurized prior to the experiments. A 300-μg sample of Cyanex 302 or 272 was added to the extraction vessel. A 10-μg sample of sodium diethyldithiocarbamate was added afterward. After the addition of 30 μL of water to the sample, the system was pressurized. A magnetic stirrer was used and set at 300 rpm. Experimental conditions were set for 20-min static extraction followed by 30-min dynamic extraction using neat CO₂ at 40 °C and 200 atm with agitation. The flow rate was measured by the pump controller, which was set at 0.5 ± 0.1 mL/min by adjusting the outlet valve. The extracted metal chelates were collected in a collection vial containing 20 mL of hexane at the exit. A heating gun was used to maintain a warm environment for the outlet valve and tubing. After phase separation, the aqueous solutions were diluted to 10 mL and subsequently analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

**Metal Extraction with CO₂ Microemulsion.** The conditions for making stable water-in-CO₂ microemulsions were investigated by the high-pressure view cell system. The surfactants (15 mM [235 mg] AOT, and 30 mM [920 mg] PFPE-PO₄) were introduced into a high-pressure view cell (volume, 16.86 mL). A certain amount of water was then added to make a desired W-value (W = [H₂O]/[surfactant], between 10 and 20). After that, the system was filled with CO₂ to a fixed pressure (100–200 atm) and temperature. The system was stirred with a magnetic stirrer for ~15 min. If a stable water-in-CO₂ microemulsion was formed, the fluid phase became optically transparent.

Changing pressure, temperature and W-value will affect the stability of the microemulsion in supercritical CO₂. For example, if pressure is reduced to the cloud point, the optically transparent solution becomes cloudy, indicating the microemulsion no longer exists due to aggregation of water and surfactants. Formation of the CO₂ microemulsion is reversible. When the pressure is increased above the cloud point, the microemulsion solution becomes transparent again. When the W-value exceeds a certain value, the optically transparent microemulsion disappears and the solution becomes cloudy at a given constant temperature and pressure.

After understanding the stability of the microemulsion system, the extraction of metals with the CO₂ microemulsion was performed using a high-pressure system shown in Figure 2. A lab coat sample spiked with metal ions was held on a stainless steel rack placed in the extraction cell. AOT and PFPE-PO₄ were added to the extraction cell. The cell was heated to 40 °C. This was followed by addition of an accurate known amount of water to make a W-value of 15, and the system was then pressurized to 200 atm and stirred to form a water-in-CO₂ microemulsion. A GC oven was used as a thermostat, and a thermocouple was used to control and monitor temperature. After a period of contact time, the system was depressurized and the fabric sample was removed from the system, treated with 2 mL of 50% HNO₃, and diluted for chemical analysis.
The residue part and samples were in triplicate runs. Calibrations were prepared using certified standards of individual solubilities of Cyanex 302 are 40 (0.13 mol L\(^{-1}\)) and 110 mol L\(^{-1}\) at 200 and 300 atm with an axially mounted torch ICP-AES was used to analyze the extracted metals. Calibration standards were run periodically through the ICP-AES analyses as quality control checks.

**Table I. In Situ Chelation/SFE\(^a\) of Metal Ions from Spiked Lab Coat Samples Using Cyanex 302, Cyanex 272, and NaDDC**

<table>
<thead>
<tr>
<th>Cyanex 302 (mg)</th>
<th>NaDDC (mg)</th>
<th>extraction efficiency (%)</th>
<th>Co</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
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<td>300</td>
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<td>0.002</td>
<td>0.004</td>
<td>0.003</td>
<td>0.003</td>
</tr>
</tbody>
</table>

\(^{a}\) SFE conditions: 10 \(\mu\)g of each element, 20-min static extraction followed by 30-min dynamic extraction at 40 °C and 200 atm with agitation. A 30-ml aliquot of water was added to the sample prior to the SFE. The extraction results were calculated based on the residue part and samples were in triplicate runs.

**Metal Analysis.** A Perkin-Elmer Optima 3000XL with an axially mounted torch ICP-AES was used to analyze the extracted metals. Calibration standards were prepared using certified standards of individual elements acquired from Aldrich Chemical Co. and Fisher Scientific. Sets of three to five different concentrations of the standards were used to establish calibration curves. To minimize matrix effects, blank and standards of known concentrations were run periodically through the ICP-AES analyses as quality control checks.

**Results and Discussion**

**SFE of Metal Species Using Organophosphorus Reagents.** The results of the experiments show that organophosphorus reagents Cyanex 302 and Cyanex 272 have good solubilities in SC-CO\(_2\) that make them suitable for SFE of trace metals.\(^{12}\) At 60 °C, the solubilities of Cyanex 302 are 40 (0.13 mol L\(^{-1}\)) and 110 g L\(^{-1}\) (0.36 mol L\(^{-1}\)) at 200 and 300 atm, respectively.\(^{12}\) The results of SFE of Co\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\), Pb\(^{2+}\), and Zn\(^{2+}\) from a spiked lab coat sample at 40 °C and 200 atm using either Cyanex 302 or 272 as an extractant are shown in Table 1: the extraction efficiencies for Co\(^{2+}\), Cd\(^{2+}\), Cu\(^{2+}\), Pb\(^{2+}\), and Zn\(^{2+}\) from the lab coat samples at 40 °C and 200 atm were 93, 91, 98, 94, and 92%, respectively. Similar results were observed when 300 mg of Cyanex 272 was mixed with 10 mg of NaDDC for SFE of metals in the same matrix. When two or more different chelating agents are used as extractants for metal species, sometimes the net extraction efficiency is enhanced. A synergistic extraction effect is well known in solvent extraction systems but has not been reported in SFE systems. The cause of synergistic extraction is often complicated, but it may be associated with the formation of a more stable and soluble complex in SC-CO\(_2\) involving two chelating agents.

The form of the Co–Cyanex 302 complex is generally CoR\(_2\)(HR), where HR is the protonated form of Cyanex 302. The metal complexes formed by Cyanex 302 have good solubilities in SC-CO\(_2\) with reasonable formation constants. At 60 °C, the solubilities of Cu–Cyanex 302 are 0.9 (2.4 \(\times\) 10\(^{-3}\) mol L\(^{-1}\)) and 7.8 g L\(^{-1}\) (2.1 \(\times\) 10\(^{-2}\) mol L\(^{-1}\)) at 200 and 300 atm, respectively.\(^{12}\) The formation constant (log \(K\)) of CdR\(_2\)(HR) was reported to be ~7.02 by Almela et al.\(^{20}\) It is known that diethylidithiocarbamate can form very stable chelates with metal ions but with low solubilities in SC-CO\(_2\).\(^{1,18}\) For example, the stability constant values (log \(K\)) for Cu(DDC)\(_2\), Cd(DDC)\(_2\), and Co(DDC)\(_2\) are 26.26, 19.22, and 15.0, respectively.\(^{18}\) The solubilities of these metal–DDC chelates in SC-CO\(_2\) are small, in the order of 10\(^{-6}\) mol/L. If a cobalt complex is formed with the two different chelating agents as shown in Figure 3, it probably would have a solubility larger than the Co(DDC)\(_2\) complex and a stability higher than the Co–Cyanex complex. This is probably the cause of the synergistic effect observed in the mixed Cyanex 302 and NaDDC system. Using a mixture of Cyanex 302 (300 mg) and Na–DDC (10 mg), near-quantitative extraction of cobalt and other metal ions spiked on the lab coat samples was achieved.

When the amount of NaDDC was increased to 2 (8.88 \(\times\) 10\(^{-6}\) mol) to 10 mg (4.44 \(\times\) 10\(^{-4}\) mol) with a fixed amount of Cyanex 302 (300 mg), the extraction efficiency increased accordingly (Table 2). With an

![Figure 3. Possible structure of a Co(II)–Cyanex 302–DDC complex.](image-url)
Table 2. Comparison of the Mixed-Ligand Effect Using Different Amounts of Dithiocarbamate Chelating Agents with a Fixed Amount of Cyanex 302*

<table>
<thead>
<tr>
<th>Cyanex 302 (300 mg) plus</th>
<th>amnt (mg)</th>
<th>amnt (mol)</th>
<th>Co</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaDDC</td>
<td>2</td>
<td>$8.88 \times 10^{-6}$</td>
<td>16 &amp; 3</td>
<td>21 &amp; 4</td>
<td>42 &amp; 8</td>
<td>42 &amp; 5</td>
<td>19 &amp; 4</td>
</tr>
<tr>
<td>NaDDC</td>
<td>5</td>
<td>$2.22 \times 10^{-5}$</td>
<td>19 &amp; 4</td>
<td>37 &amp; 7</td>
<td>45 &amp; 4</td>
<td>58 &amp; 4</td>
<td>23 &amp; 3</td>
</tr>
<tr>
<td>NaDDC</td>
<td>10</td>
<td>$4.44 \times 10^{-5}$</td>
<td>93 &amp; 5</td>
<td>91 &amp; 4</td>
<td>98 &amp; 4</td>
<td>94 &amp; 3</td>
<td>92 &amp; 3</td>
</tr>
<tr>
<td>NaDDC</td>
<td>20</td>
<td>$8.88 \times 10^{-5}$</td>
<td>94 &amp; 3</td>
<td>96 &amp; 2</td>
<td>90 &amp; 5</td>
<td>91 &amp; 3</td>
<td>90 &amp; 4</td>
</tr>
<tr>
<td>DBDC</td>
<td>2.5</td>
<td>$8.88 \times 10^{-6}$</td>
<td>46 &amp; 5</td>
<td>41 &amp; 4</td>
<td>45 &amp; 3</td>
<td>49 &amp; 4</td>
<td>43 &amp; 5</td>
</tr>
<tr>
<td>DBDC</td>
<td>6.2</td>
<td>$2.22 \times 10^{-5}$</td>
<td>42 &amp; 3</td>
<td>57 &amp; 3</td>
<td>51 &amp; 5</td>
<td>64 &amp; 4</td>
<td>59 &amp; 3</td>
</tr>
<tr>
<td>DBDC</td>
<td>12.3</td>
<td>$4.44 \times 10^{-5}$</td>
<td>89 &amp; 3</td>
<td>93 &amp; 5</td>
<td>91 &amp; 3</td>
<td>96 &amp; 4</td>
<td>91 &amp; 3</td>
</tr>
<tr>
<td>DBDC</td>
<td>24.7</td>
<td>$8.88 \times 10^{-5}$</td>
<td>91 &amp; 5</td>
<td>90 &amp; 3</td>
<td>94 &amp; 4</td>
<td>92 &amp; 4</td>
<td>93 &amp; 2</td>
</tr>
<tr>
<td>APDC</td>
<td>1.5</td>
<td>$8.88 \times 10^{-6}$</td>
<td>22 &amp; 2</td>
<td>33 &amp; 4</td>
<td>28 &amp; 3</td>
<td>23 &amp; 5</td>
<td>20 &amp; 2</td>
</tr>
<tr>
<td>APDC</td>
<td>3.6</td>
<td>$2.22 \times 10^{-5}$</td>
<td>32 &amp; 5</td>
<td>64 &amp; 3</td>
<td>23 &amp; 2</td>
<td>37 &amp; 4</td>
<td>49 &amp; 4</td>
</tr>
<tr>
<td>APDC</td>
<td>7.3</td>
<td>$4.44 \times 10^{-5}$</td>
<td>55 &amp; 3</td>
<td>66 &amp; 4</td>
<td>62 &amp; 5</td>
<td>63 &amp; 4</td>
<td>48 &amp; 5</td>
</tr>
<tr>
<td>APDC</td>
<td>14.6</td>
<td>$8.88 \times 10^{-5}$</td>
<td>84 &amp; 7</td>
<td>58 &amp; 5</td>
<td>64 &amp; 6</td>
<td>65 &amp; 3</td>
<td>49 &amp; 4</td>
</tr>
</tbody>
</table>

*SFE conditions: 10 µg of each element, 20-min static extraction followed by 30-min dynamic extraction at 40 °C and 200 atm with agitation. A 30-µL aliquot of water was added to the sample prior to the SFE Matrix, lab coat.

Figure 4. Extraction efficiency of Co and other metals using DDC with varying amounts of Cyanex 302: (●) Co, (+) Cu, (a) Cd, (●) Pb, and (C) Zn. The amount of Cyanex 302 increased from 50, 100, and 200, to 300 mg and the amount of NaDDC was fixed at 10 mg ($4.44 \times 10^{-5}$ mol). SFE conditions: 20-min static extraction followed by 30-min dynamic extraction at 40 °C and 200 atm using neat CO2 with agitation. A 30-µL aliquot of water was added to the sample prior to the SFE Matrix, lab coat.

increase in NaDDC from 10 to 20 mg ($8.88 \times 10^{-5}$ mol), the extraction efficiency did not show a detectable increase, indicating that 10 mg of NaDDC was sufficient for the mixed-ligand extraction. Other dithiocarbamate chelating agents were also tested in combination with Cyanex 302 for the extraction of the spiked metal ions from lab coat samples in SC-CO2. DBDC and APDC were chosen because both were reported in the literature as chelating agents for metal extraction in SC-CO2.16,19 Addition of DBDC ($12.3$ mg, $4.44 \times 10^{-5}$ mol) to Cyanex 302 ($300$ mg) showed about the same results as those of NaDDC + Cyanex 302 mixed system (Table 2). When APDC was added to Cyanex 302, the results were not as good as the NaDDC + Cyanex 302 mixed system.

With a fixed amount of NaDDC (10 mg), increasing Cyanex 302 tends to increase the extraction efficiency of the metals spiked in the lab coat samples. Figure 4 shows the correlation between the extraction efficiencies of the metal ions and the amount of Cyanex 302 added. With 10 mg of NaDDC, the extraction efficiencies of these metal ions increase with increasing amount of Cyanex 302 from 50 to 200 mg and reach a plateau above that. The curve for cobalt extraction with only Cyanex 302 is also given in Figure 4. The efficiency of cobalt extraction with Cyanex 302 alone is about half of that with a small amount of NaDDC (10 mg) in 200 mg of Cyanex 302.

Figure 4. Extraction efficiency of Co and other metals using DDC with varying amounts of Cyanex 302: (●) Co, (+) Cu, (a) Cd, (●) Pb, and (C) Zn. The amount of Cyanex 302 increased from 50, 100, and 200, to 300 mg and the amount of NaDDC was fixed at 10 mg ($4.44 \times 10^{-5}$ mol). SFE conditions: 20-min static extraction followed by 30 min static extraction time was set. ai 30 min followed by 30 min dynamic extraction at 40 °C and 200 atm using neat CO2 with agitation. A 30-µL aliquot of water was added to the sample prior to the SFE Matrix, lab coat.

Table 3. Recovery of Metal Ions from SFE System

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cd</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
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<tbody>
<tr>
<td>residue</td>
<td>6.2</td>
<td>1.2</td>
<td>5.1</td>
<td>4.9</td>
<td>3.2</td>
</tr>
<tr>
<td>trapped</td>
<td>74</td>
<td>93</td>
<td>93</td>
<td>90</td>
<td>92</td>
</tr>
<tr>
<td>cell + tubing</td>
<td>4.5</td>
<td>4.1</td>
<td>4.4</td>
<td>4.0</td>
<td>3.5</td>
</tr>
<tr>
<td>total</td>
<td>85</td>
<td>98</td>
<td>7</td>
<td>104</td>
<td>99</td>
</tr>
<tr>
<td>Contribution</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>98</td>
</tr>
</tbody>
</table>

*Extraction conditions: 30 µg of each element, 300 mg of Cyanex 302, and 10 mg of NaDDC in SC-CO2. T = 40 °C, P = 200 atm, static time 30 min, dynamic time 4 h, and flow rate 0.4-0.6 mL/min. Results were based on triplicate runs.

All of the results given in Table 1 and Table 2 were obtained by SC-CO2 extraction with agitation as described in the Experimental Section. According to Figure 4, over 90% of the spiked metal ions can be removed from the lab coat samples under the specified experimental conditions (200 mg of Cyanex 302 and 10 mg of NaDDC). Without agitation, the extraction efficiency for cobalt was less than 60% under the same SC-CO2 extraction conditions. Agitation appears necessary to obtain reproducible results and to enhance the extraction efficiency of metal ions in this system.

Recovery of Metal Complexes. Recovery of extracted metal complexes was studied using lab coat samples spiked with 30 µg each of Co, Cd, Cu, Pb, and Zn. The SFE conditions remained the same, i.e., 40 °C and 200 atm. Hexane was used as the trapping solvent. Flow rate was controlled around 0.5 ± 0.1 mL/min. The static extraction time was set at 30 min followed by dynamic extraction time of up to 7 h (with ~200 mL of CO2). The recovery results indicated that there was little difference if dynamic flushing time was longer than 4 h (120 mL of CO2); i.e., 4 h of dynamic flush was enough for quantitative recovery. Three portions of SFE sample, i.e., residue lab coat, trapped solution, and extraction cell and tubing, were collected and analyzed by ICP-AES. The extraction cell and tubing were washed with 50% nitric acid for ICP analysis similar to that of analyzing the lab coat sample. The majority of the metals were found in the trap solution after dynamic flushing. The lab coat sample and the walls of the cell and tubing usually contained a small percentage of metals, according to the results given in Table 3.

Several factors must also be considered for satisfactory metal recovery: (1) trapping solvent volume must be maintained at a certain level. This means a small addition of trap solvent during SFE is necessary. (2) The trap solvent should have a high solvating power for the analytes. Hexane is a good choice as a collection solvent.
in this case. (3) The outlet valve and the restrictor above the solvent should be in a warm environment in order to avoid plugging during the SFE process. In our experiments, a heating gun was used in the dynamic extraction to keep the outlet valve warm. (4) Flow rate is another factor important for satisfactory recovery of solutes. If the flow rate is too high, incomplete trapping of solutes will occur. If the flow rate is too low, poor extraction results for removing the metal ions from the solid matrix into the water core. In our experiments, the restrictor was immersed into the middle of the trap solution. Our experimental results indicate that, following the recommended conditions, quantitative recovery of the metals can be achieved. 

**Water-in-CO2 Microemulsion Extraction of Metal Species.** Recently, water-in-CO2 microemulsions have been developed for transporting polar compounds in SC-CO2. Nanometer-sized water drops can be stabilized by CO2-soluble surfactants to form microemulsions that are uniformly dispersed in SC-CO2 over an extended period of time. These surfactants are amphiphilic molecules containing a hydrophilic headgroup and a CO2-phlic tail. The tails are usually fluorinated groups, and the molecular size and shape of the head and tail are designed to favor aggregation. The size of the microemulsions depends on the molar ratio of water-to-surfactant (W) present in the SC-CO2 solution. Typically, the diameters of the spherical droplets of surfactant-encapsulated water are from a few nanometers to 50 nm. These solutions are thermodynamically stable and optically transparent since structures of this size are poor scatterers of light.

AOT is known to form stable microemulsions as reported in many water-in-oil microemulsion studies.22,23 However, microemulsions stabilized by AOT are not soluble in SC-CO2. Ji et al.24 used two surfactants, AOT and PFPE-P04, to form water-in-CO2 microemulsions. The fluorinated surfactant PFPE-P04 acts like a cosurfactant to make the AOT microemulsion soluble in SC-CO2. The AOT-PFPE-P04 surfactant used by Ji et al. has a general structure of CF3O[C=CF(CF3)2]OCF3, C2H6OCH2CH2O-P0(OH)4 and an average molecular weight of 870. Using a mixture of AOT and PFPE-P04, the resulting water-in-CO2 microemulsion is stable with W-values up to 40 at 40 °C and 200 atm.

A water-in-CO2 microemulsion can interact with metal ions in solid materials and remove them from the solid matrix into the water core. In our experiments, 235 mg (0.015 M) of AOT, 920 mg of PFPE-P04, and 182 µL of water were used to form a microemulsion in an extraction cell of 35.3 mL. The W-value was ~15. At 40 °C and 200 atm, ~40 µL of water can be dissolved in CO2, which should be subtracted from the amount of water added to the system for the W-value calculation. Lab coat samples were prepared by spiking 10 µL of a standard solution containing 1000 ppm of Co2+, Cd2+, Cu2+, Pb2+, and Zn2+. The experiments were performed at 40 °C and 200 atm with stirring.

Experimental results given in Table 4 indicate that 15 min of mixing time may not be enough for stabilizing the microemulsion and extraction of metal ions from the fabric samples. A mixing time of 30 min gave good extraction results for removing the metal ions from the matrix. To ensure a good extraction of metals from lab coat samples, 30–60 min of mixing time is needed. According to the results given in Table 4, over 90% of the spiked metal species can be extracted by the microemulsion after 1 h of mixing time. Another microemulsion extraction experiment was done with cobalt (Co2+), strontium (Sr2+), and lanthanides (La3+ and Eu3+) spiked on a lab coat sample. Blank extraction under the same conditions was also tested, which indicated that the system background was below the detection limits. In the presence of the water-in-CO2 microemulsion, effective removal of these metal ions from the fabric sample was observed. The recovery of the metal ions from the microemulsion was also investigated. In this study, 30 µg of each element were spiked on the lab coat. The system was stirred for 1.5 h for microemulsion formation and extraction. After that, the system was flushed with CO2 at 40 °C and 200 atm overnight, which usually consumed ~180 mL of CO2. The flow rate was controlled at ~0.4 mL/min, and a heating gun was used to keep the outlet valve and restrictor warm during the entire dynamic flush. The results given in Table 5 suggested that satisfactory metal ions recovery from the microemulsion system could be achieved using a long dynamic flushing.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Co (µg/g)</th>
<th>Cd (µg/g)</th>
<th>Cu (µg/g)</th>
<th>Pb (µg/g)</th>
<th>Zn (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 mL/min</td>
<td>19.2±2.4</td>
<td>18.9±2.1</td>
<td>18.5±1.9</td>
<td>18.3±1.7</td>
<td>18.1±1.5</td>
</tr>
<tr>
<td>0.2 mL/min</td>
<td>19.4±2.6</td>
<td>19.2±2.3</td>
<td>19.0±2.1</td>
<td>18.8±1.9</td>
<td>18.6±1.7</td>
</tr>
<tr>
<td>0.3 mL/min</td>
<td>19.6±2.8</td>
<td>19.4±2.6</td>
<td>19.2±2.4</td>
<td>19.0±2.2</td>
<td>18.8±2.0</td>
</tr>
</tbody>
</table>

*Conditions: 30 µg of each element, T = 40 °C, W = 15, matrix lab coat, and triplicate runs.*
~20 mL. After the washing, the cobalt remaining in the fabric was found to be 8 and 11% of the amount initially spiked on the sample based on duplicate experiments. The efficiency of conventional laundry is similar to the water-in-CO₂ microemulsion extraction, but the amount of wastewater generated in the former case is 2 orders of magnitude greater. Low levels of radionuclides in diluted aqueous solutions are usually removed by adsorption, coprecipitation, or solvent extraction and concentrated in a small volume for their final disposal.

Nuclear laundry using supercritical fluid solutions can greatly simplify the wastewater treatment procedure. Methods for disposal of radioactive wastes are known in the literature.²⁵

Conclusion

This study has demonstrated that cobalt (Co²⁺) and other metal ions spiked on a lab coat can be removed satisfactorily by a mixture of Cyanex 302 and dithiocarbamate, as well as by a water-in-CO₂ microemulsion. The efficiency of removing metal ions using either method is greater than 90%. It should be pointed out that, when treating Co²⁺-contaminated samples, the mass of the radiotracer involved is actually extremely small. Assuming each lab coat contains a total of 1 × 10⁸ Bq, the total mass of the isotope is only ~7.5–10⁻¹² mol. The cobalt concentrations tested in this study should be sufficient for treating real Co²⁺-contaminated protective coats. The microemulsion approach described in this paper does not need chelating agents. However, fluorinated surfactants required for the microemulsion formation are expensive. If inexpensive and effective surfactants for water-in-CO₂ microemulsion formation could be developed in the future, the microemulsion approach would be attractive for nuclear laundry applications. Synergistic extraction using Cyanex 302 and NaDDC is interesting for SFE of metal species. This mixed-ligand approach suggests that effective metal extractants can be developed using two ligands, one contributing to solubility and the other to stability of the resulting metal chelates in SC-CO₂. Using this approach, synthesis of stable CO₂-philic ligands such as fluorinated ligands may not be necessary. The resulting metal chelates in SC-CO₂. Using this approach, synthesis of stable CO₂-philic ligands such as fluorinated ligands may not be necessary. The resulting metal chelates in SC-CO₂. Using this approach, synthesis of stable CO₂-philic ligands such as fluorinated ligands may not be necessary. The resulting metal chelates in SC-CO₂.

Research along these directions is currently in progress.

Acknowledgment

This work was supported by DOE Office of Environmental Management, EMSP Program [Grant DE-FG07-98ER14913] and by Idaho NSF-EPSCoR Program. M.K. was on leave from Nuclear Engineering Department, Kyung-Hee University, South Korea.

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Partition Coefficients and Equilibrium Constants of Crown Ethers between Water and Organic Solvents Determined by Proton Nuclear Magnetic Resonance

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The extraction of water by several crown ethers into chloroform + carbon tetrachloride mixtures has been investigated using a proton NMR technique. The equilibrium is well described by formation of a 1:1 water–crown complex in rapid exchange with uncomplexed ligand and water. The fraction (k) of crown ether complexed with water increases with crown cavity size, varying from (15 ±1)% for 12-crown-4 to (97 ±5)% for 18-crown-6. Addition of carbon tetrachloride to chloroform lowers the k value for all crown ethers in equilibrium with water, and the value is close to zero in pure CCl₄. The partition coefficient follows the opposite trend: the amount of crown ether in the organic phase increases with the percentage of CCl₄ in this phase. The chemical shifts of free and complexed water also vary with solvent composition. Interaction of water with crown ether depends on solvation environment and may play a significant role in liquid–liquid extraction of metal ions using macrocyclic polyethers as extractants.

Introduction

Solvent extraction processes for the removal or separation of metal ions from aqueous solutions have been extensively studied using a variety of acidic, anionic, or neutral extractants. Macrocyclic compounds, such as crown ethers and calixarene-crowns, are excellent neutral extractants with high efficiency and selectivity for a number of metal cations, including the alkali metal ions. We are interested in the equilibria involved in the extraction of cesium ions from aqueous solution into a supercritical CO₂ phase, using crown ethers and calixarene-crowns. As part of this project, we are studying extraction of cesium salts into solvents of low dielectric constant, with solubility parameters in the range of possible solubility parameters for supercritical CO₂. The extraction of cesium salts with the above ligands has been studied extensively in organic solvents, usually with relatively high relative permittivity (>10). In these studies, the specific role of the water which is dissolved in the organic solvents is generally not discussed in detail. In one study, it was noted that the description of the resulting equilibria must take into account the fact that the organic phase is saturated with water. In a second study, it was found that the extraction efficiency of alkali metal ions increases with the solubility of water in the organic phase. This is ascribed to increased solubility of the counteranion in the water-saturated organic phase. In another study, the equilibrium constant between water and 18-crown-6 (18C₆) has been determined in CCl₄ by FTIR. The effects of solvent polarity on crown ether cavity size have not been discussed. Neither was the partition coefficient.

For organic solvents with a high relative permittivity, equilibration of the solvent with water yields a water concentration in the solvent which is high compared to the typical concentrations of the extracting agents and the extracted ions. Therefore, the water concentration is relatively independent of the concentrations of these other components. By contrast, the solubility of water in chloroform (relative permittivity 4.8 at 20 °C) is about 0.06 mol·L⁻¹ at normal ambient temperature, which is more comparable to the concentrations of other species extracted from a water phase. Water solubility varies from 0.02 to 0.2 mol·L⁻¹ in supercritical CO₂, depending on the temperature and the pressure applied.

Proton nuclear magnetic resonance (NMR) is a very precise analytical technique for measuring the amount and chemical environment of water in organic solvents. Early NMR studies by de Jong et al. and Golovkova et al. have shown that various crown ethers interact with water to form 1:1 complexes in CHCl₃. An NMR study by Moyer et al. has likewise demonstrated formation of a 1:1 water–crown ether complex in CCl₄. A compilation of data for complexes of crown ethers with neutral molecules has been carried out by Izatt et al.

The purpose of this paper is to determine the influence of solvent (mixtures of CHCl₃ and CCl₄) on these interactions using NMR techniques. These solvent mixtures cover a wide range of solvent parameters which are comparable to those of liquid and supercritical CO₂ at different densities. Some of the crown ethers used in this study are appreciably soluble in water, leading to their partitioning between the water and organic phases. NMR measurements also enable us to obtain partition coefficients of crown ethers between water and organic phases.

Experimental Section

The crown ethers dibenzyl-24-crown-8 (DB24C₈), dicyclohexano-24-crown-8 (DCH24C₈), dicyclohexano-18-crown-6 (DCH18C₆), 12-crown-4 (12C₄), 15-crown-5 (15C₅), and 18-crown-6 (18C₆) were purchased from Aldrich Chemical Co. and used without further purification. To carry out the NMR measurement, chloroform was used in its deuterated form (99.5% CDCl₃). The water phase contained 5% D₂O by volume.

Solutions of the crown ethers, in the concentration range (0.02 to 0.2) mol·L⁻¹, in the CDCl₃ + CCl₄ mixtures were
The concentrations of 18-crown-6 after equilibration with water were determined with a CDC13 field lock. The intensity (based on integrated phase on the basis of NMR measurements of its partition in CDC13) was set at 7.15 ppm. The ratios were within the range (25 ± 1) °C.

NMR measurements for the solvent experiments were carried out using a 500 MHz Bruker DRX500 spectrometer. To obtain quantitative results, the pulse interval was set to 11.3 s (acquisition time 3.3 s, relaxation delay 8 s) and the pulse width was 30° (corresponding to a 2 µs relation time) in all systems (organic, aqueous, with or without chelator agent). Chemical shifts in the organic phase were calibrated by setting the chloroform chemical shift to 7.24 ppm. For the solvent mixtures containing CC14, the chloroform resonance shifts upfield (lower ppm) as CC14 is added. The magnitude of this effect was measured by comparing the solvent mixtures at constant field, that is, with the field lock turned off. The shift between 100% CHCl3 and 25% CHCl3 was 0.14 ppm. Therefore, an upfield correction was added for the mixed solvent samples run in a CDC13 field lock. The intensity (based on integrated area calculations for all data) of the water peaks in the NMR spectra was corrected for the 5% D2O (by volume) present in the water phase. For the 100% CC14 mixture, an insert filled up with benzene-C6 has been used as a reference for the intensity and the chemical shift, which was set at 7.15 ppm.

Typical NMR spectra for 18C6 in the CDC13 phase are shown in Figure 1. For the unsubstituted crown ethers, there is only a single resonance for the ring protons, generally in the region between (3 and 4) ppm. A singlet resonance for water appears at a chemical shift which moves downfield as the ligand concentration is increased. As noted above, the observed water and ligand-resonances are averages which result from the rapid equilibrium between uncomplexed ligand and water and the complex L·H2O(org). Figure 1 shows the trend of the chemical shift for the water resonance associated with 18C6 concentration in CDC13. The concentration of the ligand in the organic phase has been corrected for its solubility in the aqueous phase on the basis of NMR measurements of its partition between the two phases.

The purities of the substituted crown ethers were assessed by determining the relative areas of the various resonances of the crown ethers, under conditions such that there is no overlap with the water peak. The ratios agreed with the theoretical values to better than 1%. All spectra were relatively free of artifacts, indicating a purity of crown ethers of 99% or better.

**Calculations**

The equilibrium model for the extraction is straightforward. Representing the crown ether ligand by L and the organic phase by (org), we have

\[
\text{H}_2\text{O}_{(\text{org})} \leftrightarrow \text{H}_2\text{O}_{(\text{org})} + \text{L} \quad (1)
\]

\[
\text{L}_{(\text{org})} \leftrightarrow \text{L}_{(\text{org})} + \text{H}_2\text{O}_{(\text{org})} 
\]

\[
\text{H}_2\text{O}_{(\text{org})} + \text{L}_{(\text{org})} \leftrightarrow \text{L} \cdot \text{H}_2\text{O}_{(\text{org})} 
\]

where \(\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}\) represents a ligand-water complex. We define

\[
K = \frac{[\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}][\text{H}_2\text{O}_{(\text{org})}]}{[\text{L}_{(\text{org})}][\text{H}_2\text{O}_{(\text{org})}]} 
\]

(4)

to be the equilibrium constant corresponding to eq 3 on the basis of concentrations ([ ], in mol·L⁻¹). Because of equilibrium 1, the concentration \([\text{H}_2\text{O}_{(\text{org})}]\) is independent of the ligand concentration. Therefore, the ratio \([\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}]/[\text{L}_{(\text{org})}]\) is independent of the ligand concentration. Likewise, \(k\), the fraction of ligand molecules complexed to water as defined in eq 5 is independent of the ligand concentration.

\[
k = \frac{[\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}]}{[\text{L}_{(\text{org})}]} 
\]

(5)

When \([\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}]\) is expressed in terms of \(K[\text{L}_{(\text{org})}][\text{H}_2\text{O}_{(\text{org})}]\), the constant \(k\) is related to \(K\) by

\[
k = K[\text{H}_2\text{O}_{(\text{org})}]/(1 + K[\text{H}_2\text{O}_{(\text{org})}]) 
\]

(6)

The initial total ligand concentration \([\text{L}_{(\text{org})}]\) is calculated from the total mass of ligand dissolved in a known volume of the organic phase during the preparation of the solutions. By material balance, at equilibrium

\[
[\text{L}_{(\text{org})}] = [\text{L}_{(\text{org})}'] + [\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}] 
\]

(7)

For the crown ethers containing additional organic groups (benzyl and cyclohexyl), the term \([\text{L}_{(\text{org})}]\), representing extraction of the ligand into the aqueous phase, is negligible. Because of the rapid exchange of complexed and uncomplexed water in the organic phase, only the totals

\[
[\text{L}_{(\text{org})}] = [\text{L}_{(\text{org})}'] + [\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}] 
\]

(8)

and

\[
[\text{H}_2\text{O}_{(\text{org})}] = [\text{H}_2\text{O}_{(\text{org})}'] + [\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}] 
\]

(9)

can be measured directly, where \([\text{H}_2\text{O}_{(\text{org})}]\) and \([\text{L}_{(\text{org})}]\) are the total concentrations of water (uncomplexed and complexed water) and ligand (free and complexed ligand) present in the organic phase, respectively.

When the material balance relations (eqs 8 and 9) are combined with eq 5, the linear relation

\[
[\text{H}_2\text{O}_{(\text{org})}] = k[\text{L}_{(\text{org})}'] + [\text{H}_2\text{O}_{(\text{org})}'] 
\]

(10)

can be derived. According to eq 10, a plot of \([\text{H}_2\text{O}_{(\text{org})}]\) versus \([\text{L}_{(\text{org})}]\) should yield a straight line and the slope gives the value \(k\). From \(k\) and \([\text{H}_2\text{O}_{(\text{org})}]\), the equilibrium constant \(K\) can be obtained from eq 6.

As noted above, the equilibrium between \(\text{H}_2\text{O}_{(\text{org})}\) and \(\text{L} \cdot \text{H}_2\text{O}_{(\text{org})}\) determines the observed NMR chemical shift \(\delta\) of
were done by adding a known amount of CNC13 to CDC13 water in chloroform. Denoting δ₉ = the chemical shift of pure water in the organic solvent and δ₁ = the chemical shift of complexed water, we have

\[
\frac{(\delta - \delta_0)}{(\delta_1 - \delta_0)} = \frac{[L \cdot H₂O_{(org)}/[H₂O_{(org)}]}{[L \cdot H₂O_{(org)}/[H₂O_{(org)}]} \quad (11)
\]

Combining eq 11 with eqs 6 and 8 and rearranging produces the linear relation between δ and \([L_{(org)}]/[H₂O_{(org)}] \)

\[
\delta = \delta_0 + k(\delta_1 - \delta_0)[L_{(org)}]/[H₂O_{(org)}] \quad (12)
\]

According to eq 12, \(\delta_0\) and \(\delta_1\) can be determined by linear regression once \(k\) is known.

The NMR data required for obtaining equilibrium (\(k\) and \(K\)) and chemical shift parameters (\(\delta_0\) and \(\delta_1\)) are the intensities of the water and the ligand peaks ([H₂O_{(org)}] and \([L_{(org)}]\) and the chemical shift (δ) of the water peak in the organic phase. For the NMR intensity measurements, the water peak in the aqueous phase or the CHCl₃ peak in the organic phase can be used as the reference. At 25 °C, the density of water is known and the concentration of 95% water by volume is 52.8 mol.L⁻¹. Using the CHCl₃ peak as the reference, the amount of CHCl₃ in CDC₁₃ must be known. The results represented in Table 1 were obtained using the water peak as the reference. A few experiments were done by adding a known amount of CHCl₃ to CDC₁₃ as the reference. The results are consistent with those obtained using the water peak as the reference within the experimental uncertainty. The intensities of the ligand peaks in the aqueous phase were also measured to evaluate their partition coefficients (D) and for correction of ligand concentrations in the organic phase.

It should be noted that eq 12 differs from the classic complex equilibrium equations derived from the work of Benesi and Hildebrand²⁰ and Deranleau,²¹ which are derived for a single-phase system containing two interacting components. As pointed out in the Calculations section, because of equilibrium 1, [H₂O_{(org)}] is constant. As an incidental consequence, [H₂O_{(org)}] cannot go to zero. This enables an extrapolation of eq 12 to zero ligand concentration and \(D_{\text{eq}}\) to get the value of \(D_0\). Also, two separate quantities [H₂O_{(org)}] and \([L_{(org)}]\) appear which vary together, since increasing [H₂O_{(org)}] increases \([L_{(org)}]\). Unlike the case in the previous work, none of the individual species can be known.

Table 1. Equilibrium and Chemical Shift Parameters of Various Crown Ethers

<table>
<thead>
<tr>
<th>crown</th>
<th>% vol CDC₁₃</th>
<th>(k)</th>
<th>(K) [L mol⁻¹]</th>
<th>([H₂O_{eq}])</th>
<th>(D_{eq})</th>
<th>(\delta_0) ppm</th>
<th>(\delta_1) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>12C₄</td>
<td>100</td>
<td>0.15</td>
<td>2.78</td>
<td>0.065</td>
<td>0.25</td>
<td>1.55</td>
<td>3.0</td>
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<tr>
<td></td>
<td>75</td>
<td>0.10</td>
<td>2.79</td>
<td>0.039</td>
<td>0.34</td>
<td>1.43</td>
<td>3.0</td>
</tr>
<tr>
<td>15C₅</td>
<td>100</td>
<td>0.54</td>
<td>25.6</td>
<td>0.045</td>
<td>0.18</td>
<td>1.49</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.35</td>
<td>19.9</td>
<td>0.027</td>
<td>0.29</td>
<td>1.40</td>
<td>2.7</td>
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<td></td>
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<td>0.25</td>
<td>14.2</td>
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<td>0.71</td>
<td>1.29</td>
<td>2.8</td>
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<td></td>
<td>25</td>
<td>0.21</td>
<td>35</td>
<td>0.008</td>
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<td>1.11</td>
<td>2.0</td>
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<td></td>
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<td></td>
<td></td>
<td>0.00²</td>
<td>2.450</td>
<td>1.36</td>
<td></td>
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<td>18C₆</td>
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<td>0.97</td>
<td>545</td>
<td>0.060</td>
<td>0.25</td>
<td>1.52</td>
<td>3.1</td>
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<tr>
<td></td>
<td>50</td>
<td>0.63</td>
<td>97</td>
<td>0.017</td>
<td>1.16</td>
<td>1.28</td>
<td>2.6</td>
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<td></td>
<td>25</td>
<td>0.61</td>
<td>141</td>
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<td></td>
<td></td>
<td>0.00²</td>
<td>48.04</td>
<td>1.31</td>
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<tr>
<td>DCH18C₆</td>
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<td>0.70</td>
<td>32</td>
<td>0.072</td>
<td>0.00</td>
<td>1.52</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.58</td>
<td>81</td>
<td>0.017</td>
<td>0.00²</td>
<td>1.25</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.40</td>
<td>36</td>
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<td>0.00²</td>
<td>1.13</td>
<td>2.6</td>
</tr>
<tr>
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<td>0</td>
<td></td>
<td></td>
<td>0.00²</td>
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<td>1.57</td>
<td>2.7</td>
</tr>
<tr>
<td>DCH24C₈</td>
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<td>0.85</td>
<td>93</td>
<td>0.060</td>
<td>0.00²</td>
<td>1.57</td>
<td>3.2</td>
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<tr>
<td></td>
<td>100</td>
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<td>9.03</td>
<td>0.064</td>
<td>0.00²</td>
<td>1.57</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*Typical statistical errors (based on linear regressions): \(k\) ± 5%; \(K\) ± 1.1%; \([H₂O_{eq}]\) ± 0.003 mol.L⁻¹; \(D\) ± 5%; \(\delta_0\) ± 0.04 ppm; \(\delta_1\) ± 1.0 ppm. \(^{2}\)Volume percentage of CDC₁₃ in CDC₁₃. \(^{3}\)Concentration in moles per liter. \(^{4}\)For the ligand concentration range 0.02–0.2 mol.L⁻¹.

**Results and Discussion**

Parts a and b of Figure 2 show plots based on eqs 10 and 12, respectively, for 18C₆ in CDC₁₃. Results for the other ligands are similar. The linear relations obtained in every case verify that the water–ligand equilibrium is well described by formation of a 1:1 complex. Figure 2a yields a slope of 0.970 ± 0.04 (corresponding to \(D\)) and an intercept...
of 0.060 \pm 0.003 (corresponding to [H₂O]₉-org) based on our regression analysis \((R^2 = 0.991)\) and according to eq 10. The free (uncomplexed) water dissolved in chloroform is about 0.06 mol-L⁻¹ for the H₂O + CHCl₃ + 18C₆ system at room temperature (25 \(\pm 1\) °C). This value is confirmed by the analysis of a solution of water saturated chloroform-

The concentration of the total water in the organic phase, [H₂O]₉-org + L[H₂O]₉-org, depends on the ligand concentration as shown in Figure 2a. About 97% of the ligands in the organic phase are complexed with water. The 

Figure 3. Determination of the partition coefficient for 18-crown-6 in (○) CDCl₃, (▲) 50% CDCl₃ + CCl₄, and (●) CCl₄.

Results for the equilibrium and NMR chemical shift parameters for the six crown ethers studied by this work are summarized in Table 1. In CDCl₃, the \(k\) values for unsubstituted crown ethers 12C₄, 15C₅, and 18C₆ are 0.15, 0.54, and 0.97, respectively. This trend shows strong binding of water for 18C₆ relative to the smaller rings. Substitution in crown ethers tends to lower the \(k\) value. Thus, for DCH₁₈C₆, the \(k\) value in chloroform is lowered to 0.70 compared with a value of 0.97 for the unsubstituted 18C₆. In the case of DCH₂₄C₈ and DB₂₄C₈, benzyl substitution further lowers the \(k\) value compared with cyclohexyl substitution in 24C₈. The equilibrium constant \(K\) defined by eq 4 varies from 2.78 for 12C₄ to 545 for 18C₆ in chloroform. The \(K\) value for the substituted (DCH₁₈C₆) crown is much lower than that of the unsubstituted (18C₆) one (32 versus 545). The \(\delta_0\) values for the three unsubstituted crown ethers are approximately constant (in the range 1.53 \(\pm 0.04\) ppm), as expected. Considering the experimental error, the \(\delta_1\) value is stable.

For the individual ligands, there are several clear trends with respect to the variation of solvent composition (CDCl₃ + CCl₄). First, the amount of free water dissolved in the organic phase decreases with increasing CCl₄ fraction in the solvent. This is expected, since decreasing the solvent polarity should result in lower solubility of water in the organic phase. In all cases, the parameter \(k\) representing the fraction of ligand bound to water also decreases monotonically as the proportion of CCl₄ increases. Thus, decreasing solvent polarity also reduces water–crown complexation \([L-H₂O]_{org}\) leading to lower \(k\) values. This probably caused by the combination of a lower solubility of free water in the organic phase and intrinsic solvation effects on the crown–water complex. The equilibrium constant \(K\), which includes the concentration of unbound water and the ligand in the mixed organic phase, changes less and in an irregular fashion. Because both [H₂O]₉-org and \([L]_{org}\) vary drastically with the solvent composition, the \(K\) values defined by eq 4 are not as useful as the \(k\) values for discussion in the CHCl₃ + CCl₄ system. In the binary solvent systems, [H₂O]₉-org decreases with increasing CCl₄ fraction whereas \([L]_{org}\) changes independently in the opposite direction, resulting in irregular trends for the \(K\) values.

From the crown ether NMR peak intensities in the organic and in the aqueous phases, we also calculated the partition coefficients \(D = \frac{[L]_{org}}{[L]_{org}}\) as shown in Table 1. The \(D\) values for 12C₄ and 18C₆ between water and chloroform are around 0.25, and that for 15C₅ is somewhat lower. For the crown ethers that are appreciably soluble in water, the partition coefficients show that extraction into the aqueous phase increases exponentially as the organic solvent polarity decreases. In the case of 18C₆, the \(D\) value starts at 0.25 in 100% CHCl₃, becomes 1.16 with a 50:50 mixture of CHCl₃ and CCl₄, and rises up to 48 for a 100% CCl₄ solution (Figure 3). For the substituted crown ethers DCH₂₄C₈, DCH₂₄C₈, and DB₂₄C₈, the \(D\) values are below detection (<0.01) in the concentration range (0.06 to 0.2) mol-L⁻¹. Partitioning of 18-crown-6 between water and various organic solvents has been determined by several different methods including gravimetric and conductivity measurements.17–19 NMR actually provides a simple and rapid method for determination of crown ether partition coefficients between water and organic solvents. The \(D\) values given in Table 1 represent the first systematic measurements of such data using a NMR technique.

The NMR studies performed by Golovkova et al.15 in CDCl₃ investigated several compounds also covered in our work (15C₅, 18C₆, and DCH₁₈C₆). In their work, single-phase measurements were made with a constant water concentration and varying ligand concentrations. Analysis was based on the chemical shift employing eq 11. The chemical shift \(\delta_0\) for the pure complex \(L\cdot H₂O\) was determined by extrapolation to infinite ligand concentration. Their results for \(K\) deviate widely from ours, sometimes by an order of magnitude. We feel that their extrapolation method is subject to considerable error because (1) the dependence of the chemical shift on ligand concentration is nonlinear and, (2) on the basis of the \(\delta_1\) values we obtained, the range of concentrations they employed was insufficient. Our calculational method involved only the use of linear regression analysis; thus, it is more accurate.

The chemical shifts \(\delta_0\) representing isolated water molecules in the organic solvent, can be measured by equilibrating the organic solvent with pure water. For 18C₆, the \(\delta_0\) values decrease from 1.56 ppm in pure chloroform to 1.08 ppm in the CHCl₃ + CCl₄ mixture with 25% CHCl₃ by volume. Similar trends are observed for the other crown ether systems. For 15C₅ and DCH₁₈C₆, the \(\delta_0\) values decrease, respectively, from 1.49 ppm to 1.52 ppm in pure chloroform and from 1.11 ppm to 1.08 ppm in the CHCl₃ + CCl₄ mixture with 25% CHCl₃ by volume. Those results follow the general trend of an upfield shift for water in solvents of decreasing polarity. The values of \(\delta_0\) and \(\delta_1\) in Table 1 were found using a linear regression plot of \(\delta\) versus \([L]_{org}/[H₂O]_{org}\) according to eq 12 and using the \(k\) values predetermined. Those results agree well with preceding measurements involving no crown ethers.
$\delta_1$ represents the chemical shift of water in the crownwater complex. The error on $\delta_1$ values includes the error on $k$; therefore, the $\delta_1$ value is less accurate than the $\delta_0$ one. In the 18C6 series, $\delta_1$ decreases monotonically with decreasing solvate polarity from $3.1$ ppm in pure chloroform to $2.2$ ppm in the CHCl$_3$ + CCl$_4$ mixture with $25\%$ CHCl$_3$ by volume. The trends of $\delta_1$ for the other crown ethers are less clear. Generally, there is an upfield shift as the solvent polarity decreases. This does not seem obvious, however, for the weakly binding ligands 12C4 and 15C5.

Complexation of water with crown ether depends strongly on the nature of the solvents. The difference in solvation environment of chloroform and carbon tetrachloride is reflected in the degree of crown-water complexation and the chemical shifts of free water and the crown-water complex described in this NMR study. Interaction between water and crown ether is likely to affect complex formation of the crown ether with metal ions during liquid–liquid extraction. Crown ethers have been extensively investigated for selective extraction of the alkali metal and the alkali earth metal ions from aqueous solutions. The solvation effects of water and solvent molecules on metal-crown complexation are not well understood. NMR studies may provide useful information for understanding such interactions. Solvation effects can be studied using different conventional solvents. Conventional solvents offer discontinued changes in solvation environment and often involve other variables that are difficult to control experimentally. Further studies of water–crown interactions in a system with a tunable solvation environment, supercritic fluid carbon dioxide, are currently in progress in our laboratory.

**Literature Cited**


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Characterization of a Tri-\textit{n}-butyl Phosphate–Nitric Acid Complex: a CO\textsubscript{2}-Soluble Extractant for Dissolution of Uranium Dioxide

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Tri-\textit{n}-butyl phosphate (TBP) reacts with nitric acid to form a hydrogen-bonded complex TBP-(HNO\textsubscript{3})\textsubscript{x}(H\textsubscript{2}O\textsubscript{y}), that is highly soluble in supercritical fluid carbon dioxide (SF-CO\textsubscript{2}). The value of \(x\) can be up to 2.5, whereas the value of \(y\) varies between 0.4 and 0.8 determined by acid–base and Karl Fischer titrations. The protons of HNO\textsubscript{3} and H\textsubscript{2}O in the complex undergo rapid exchange and exhibit a singlet resonance peak in NMR spectra. When the complex is dissolved in a low dielectric constant solvent, small droplets of nitric acid are formed that can be detected by NMR. Phase behavior studies indicate that the complex forms a single phase with SF-CO\textsubscript{2} above a certain pressure for a given temperature. This CO\textsubscript{2}-soluble Lewis acid–base complex provides a method of introducing nitric acid in SF-CO\textsubscript{2} for effective dissolution of uranium dioxide, lanthanide oxides, and perhaps other metal oxides.

Introduction

Recent reports show that tri-\textit{n}-butyl phosphate (TBP) forms a solution with nitric acid that is soluble in supercritical fluid carbon dioxide (SF-CO\textsubscript{2}) and capable of dissolving lanthanide oxides and uranium oxides.\textsuperscript{1}–\textsuperscript{5} The ability of this CO\textsubscript{2}-philic TBP-nitric acid solution to dissolve solid uranium dioxide (UO\textsubscript{2}) directly in SF-CO\textsubscript{2} suggests a potential new technique for reprocessing of spent nuclear fuels and for treatment of nuclear wastes. The UO\textsubscript{2} dissolution process in SF-CO\textsubscript{2} probably involves oxidation of the tetravalent U in UO\textsubscript{2} to the hexavalent (UO\textsubscript{2})\textsuperscript{2+} by nitric acid followed by formation of UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·2TBP.\textsuperscript{4} The product UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·2TBP identified from the supercritical fluid dissolution process is known to have a very high solubility in CO\textsubscript{2}.\textsuperscript{6,7}

In the conventional Purex (plutonium–uranium extraction) process, aqueous nitric acid (3–6 M) is used to dissolve and oxidize UO\textsubscript{2} in the spent fuel to uranyl ions ([UO\textsubscript{2}]\textsuperscript{2+}). The acid solution is then extracted with TBP in an organic solvent such as dodecane to dissolve uranium as UO\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}·2TBP into the organic phase.\textsuperscript{8} Direct dissolution of solid UO\textsubscript{2} in SF-CO\textsubscript{2} with a TBP–nitric acid complex obviously has an advantage over the conventional Purex process because it would combine dissolution and extraction steps into one with a minimum waste generation. Demonstration of this super-DIREX process (supercritical fluid direct extraction process) is currently underway in Japan involving Mitsubichi Heavy Industries, Japan Nuclear Cycle Corp., and Nagoya University. The project is aimed at extracting uranium and plutonium from the mixed oxide fuel as well as the irradiated nuclear fuel using a TBP-nitric acid complex in SF-CO\textsubscript{2}.

The chemical nature of the TBP–nitric acid complex and the mechanisms of UO\textsubscript{2} dissolution in SF-CO\textsubscript{2} with the TBP–nitric acid solution are not well-known. The TBP–nitric acid complex is prepared by shaking TBP with a concentrated nitric acid solution. Because water is present in the nitric acid solution, the complex is expected to have a general formula of TBP-(HNO\textsubscript{3})\textsubscript{x}(H\textsubscript{2}O\textsubscript{y}), where \(x\) and \(y\) can vary depending on the relative amounts of TBP and nitric acid used in the preparation. Two types of the complexes, one with \(x = 0.7\) and the other with \(x = 1.8\), were reported in the literature for direct dissolution of uranium dioxide in SF-CO\textsubscript{2}.\textsuperscript{3}–\textsuperscript{5} In the former case with a HNO\textsubscript{3}/TBP ratio of 0.7, the complex was found to cause cloudiness of the supercritical fluid phase, indicating formation of small acid water droplets released from the complex probably as a result of an antisolvent effect of SF-CO\textsubscript{2}.\textsuperscript{4}

The solubility of water in pure TBP at room temperature is about 64 g/L of the solution, which is close to a 1:1 molar ratio of TBP:H\textsubscript{2}O. In the TBP–H\textsubscript{2}O binary system, water is most likely bound to TBP through hydrogen bonding with phosphoryl oxygen, forming a 1:1 complex. The bonding between TBP and H\textsubscript{2}O in the presence of HNO\textsubscript{3} is unknown. Recent molecular dynamics investigations suggest that hydronium ions or hydrogen from HNO\textsubscript{3} or H\textsubscript{2}O are bonded to the oxygen of the P=O bond in TBP.\textsuperscript{9,10} Knowledge on the equilibrium compositions of the TBP(HNO\textsubscript{3})\textsubscript{x}(H\textsubscript{2}O\textsubscript{y}) complex prepared by different proportions of the initial TBP and nitric acid is essential for understanding the nature and mechanisms of UO\textsubscript{2} dissolution in SF-CO\textsubscript{2}.

In this paper, we report our initial results of characterizing the TBP(HNO\textsubscript{3})\textsubscript{x}(H\textsubscript{2}O\textsubscript{y}) complex using several different methods including the Karl Fischer method for water determination, conventional acid–base titration for measurement of HNO\textsubscript{3}, nuclear magnetic resonance (NMR) spectroscopy to evaluate chemical environments...
of protons, and visual observation of the phase behavior of the complex in SF-CO₂.

Experimental Section

TBP was purchased from Avocado (ordered through Alfa Aesar, Ward Hill, MA). Nitric acid [69.5% (w/w)] was obtained from Fisher Chemical (Fair Lawn, NJ) and was diluted to 15.5 M by deionized water. The TBP-(HNO₃)ₓ(H₂O)ᵧ complex was prepared by mixing 98% TBP with 15.5 M nitric acid at a chosen ratio in a glass tube with a stopper. The mixture of TBP and nitric acid was manually shaken vigorously for 4 min, followed by centrifuging for 1 h. After phase separation, portions of the TBP phase and the aqueous phase were removed with pipets for characterization experiments.

The concentration of H₂O in the TBP phase was measured by Karl Fischer titration using an Aquacounter AQ-7 instrument (Hiranuma, Japan). The concentration of HNO₃ in the TBP phase was measured with an automatic titrator (COM-450, Hiranuma, Japan) with a 0.1 M NaOH solution after adding an excess amount of deionized water to the organic phase. A typical procedure is by shaking 1 mL of the TBP phase with 50 mL of water. After phase separation, the amount of nitric acid in the aqueous phase was determined by NaOH titration. A 500 MHz NMR spectrometer (Bruker Advance 500) was used for proton NMR (PNMR) measurements. The phase behavior was studied using a high-pressure view-cell system purchased from Taiatsu Techno Co. (Tokyo, Japan) and a video camera.

Results and Discussion

1. Characterization of the TBP(HNO₃)ₓ(H₂O)ᵧ Complex by Titration Methods. The amount of HNO₃ in the complex was evaluated by the acid–base titration method described in the Experimental Section. Figure 1 shows the acidity of the TBP phase (organic phase) with respect to the initial nitric acid/TBP ratio. The organic phase acidity (closed circles) and the acidity of the equilibrated aqueous phase (open circles) are shown in Figure 1. A significant fraction of the HNO₃ in the initial acid solution can be incorporated into the TBP phase, resulting in an acidity of the organic phase greater than 3 M for all of the cases shown in Figure 1. If the initial volume ratio of nitric acid/TBP is unity or higher, the acidity of the TBP phase exceeds 6 M. The high acidity carried by the TBP phase is important for dissolving uranium dioxide, lanthanide oxides, and perhaps other metal oxides in SF-CO₂.

When the molar ratio of HNO₃/TBP in the organic phase is plotted against the molar ratio of HNO₃/H₂O in the equilibrated aqueous phase, the experimental data appear to show two regions with a breaking point of around unity for the HNO₃/TBP ratio (Figure 2). The data seem to suggest that there are two types of the TBP(HNO₃)ₓ(H₂O)ᵧ complex. The type I complex would incorporate HNO₃ rapidly into the TBP phase until a 1:1 ratio of HNO₃/TBP is reached. Beyond that point, there is another region where incorporation of HNO₃ into TBP becomes slow. According to Figure 2, more than two molecules of HNO₃ can be associated with each TBP molecule in the complex if the organic phase is equilibrated with a concentrated nitric acid. TBP is a highly CO₂-soluble Lewis base. Inorganic acids such as nitric acid, which are usually insoluble in CO₂, can be made soluble by complexation with a CO₂-soluble Lewis base such as TBP. This Lewis acid–base complex approach may provide a method of dispersing various CO₂-insoluble acids in the SF-CO₂ phase for chemical reactions.

The amount of water in the TBP(HNO₃)ₓ(H₂O)ᵧ complex determined by the Karl Fischer method also shows two distinct regions. When the molar ratio of HNO₃/H₂O in the TBP phase is plotted against the molar ratio of HNO₃/H₂O in the equilibrated aqueous phase, it clearly shows two different types of the TBP-(HNO₃)ₓ(H₂O)ᵧ complex (Figure 3). In region I, the ratio of HNO₃/H₂O in the TBP phase tends to increase with increasing HNO₃/H₂O ratio in the aqueous phase. In region II, the ratio of HNO₃/H₂O in the TBP phase maintains a constant value of about 3 with increasing HNO₃/H₂O ratio in the equilibrated aqueous phase. The ratio of HNO₃/TBP in the organic phase continues to increase with increasing HNO₃/H₂O ratio in the aqueous phase as shown in Figure 2, but the ratio of HNO₃/H₂O in the organic phase remains a constant. It appears that, for the type II complex, the nitric acid incorporated into the TBP phase is in a form with a general formula of 3HNO₃·H₂O.

2. Characterization of the Complex by PNMR Spectroscopy. PNMR spectra of the TBP(HNO₃)ₓ(H₂O)ᵧ complex at room temperature were taken using an insert technique. Deuterated water (D₂O) was placed
Figure 3. Molecular ratio of $[\text{HNO}_3]/[\text{H}_2\text{O}]$ in the TBP phase versus that in the equilibrated aqueous phase.

Figure 4. Typical PNMR spectrum of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ with a D$_2$O insert. The sample was prepared by mixing 1.0 mL of 15.5 M HNO$_3$ with 4.0 mL of 98% TBP.

Figure 5. Chemical shift of the H$_2$O proton peak (in ppm) with respect to the molar ratio of HNO$_3$/TBP in TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$.

Figure 6. PNMR spectrum of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ in CDC$_3$. The complex was prepared by mixing 4 mL of TBP and 1 mL of 15.5 M HNO$_3$; volume ratio of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ to CDC$_3$ = 1:1.

Figure 7. PNMR spectrum of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ in CDC$_3$. The complex was prepared by mixing 4 mL of TBP and 1 mL of 15.5 M HNO$_3$; volume ratio of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ to CDC$_3$ = 1:1.

A typical PNMR spectrum of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ with a D$_2$O insert is shown in Figure 4. The singlet peak at 11.80 ppm corresponds to the protons of HNO$_3$ and water in the TBP phase. H$_2$O in a TBP–H$_2$O complex sample shows a singlet resonance peak at 3.85 ppm. In the TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ system, this singlet peak shifts upfield with increasing HNO$_3$ in the system. The NMR shift is attributed to a rapid exchange between the protons of H$_2$O and those of HNO$_3$ in the complex. A series of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ samples prepared from a different volume ratio of TBP/HNO$_3$ (15.5 M) were studied. All NMR spectra in this series of samples showed a singlet peak for the protons corresponding to HNO$_3$ and H$_2$O. The PNMR shift of the HNO$_3$–H$_2$O singlet peak with respect to the molar ratio of HNO$_3$/TBP in the complex is shown in Figure 5. The chemical shift increases rapidly as the fraction of HNO$_3$ in the TBP phase increases in the region where the molar ratio of HNO$_3$/TBP is less than unity. The chemical shift of this peak approaches a constant when the HNO$_3$/TBP ratio in the complex is greater than 1. The two regions of the chemical shift observed from the PNMR spectra support the titration results shown in Figure 3, i.e., there are probably two types of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ depending on the HNO$_3$/TBP ratio in the complex.

NMR experiments to study the antisolvent effect of SF–CO$_2$ on the TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ complex are difficult to carry out at the present time because of the corrosive nature of the solute and the lack of a safe high-pressure NMR device in our laboratory. We chose to use chloroform (CDC$_3$) to evaluate the antisolvent effect because chloroform has a small dielectric constant at room temperature ($\varepsilon = 4.81$ at 20°C). Two TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ complexes were prepared with the following mixtures: (i) 4 mL of TBP and 1 mL of 15.5 M HNO$_3$ and (ii) 2 mL of TBP and 2 mL of 15.5 M HNO$_3$. The PNMR spectra of these two TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ complexes in CDC$_3$ are given in Figures 6 and 7. Both PNMR spectra show two peaks in addition to the protons in the butyl group of TBP. The peak at 6.49 ppm in Figure 6 and the peak at 8.13 ppm in Figure 7 are the peaks belonging to the nitric acid droplets formed in the system. The nitric acid droplets are not dissolved in the CDC$_3$ solution. These peaks were identified by a separate NMR study using different concentrations of nitric acid mixed with CDC$_3$. The nitric acid peak in CDC$_3$ tends to shift upfield with increasing HNO$_3$ concentration in the acid solution. The peak at 12.49 ppm in Figure 6 and the peak at 12.09 ppm in Figure 7 are the peaks representing the averaged protons of HNO$_3$ and H$_2$O in the complex. The NMR results obtained from the CDC$_3$–TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ system, though qualitative in nature, demonstrate the formation of nitric acid droplets from the

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\begin{align*}
\text{Figure 3. Molecular ratio of } [\text{HNO}_3]/[\text{H}_2\text{O}] \text{ in the TBP phase} \\
&\text{versus that in the equilibrated aqueous phase.} \\
\text{Figure 4. Typical PNMR spectrum of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ with a} \\
&\text{D$_2$O insert. The sample was prepared by mixing 1.0 mL of 15.5 M} \\
&\text{HNO$_3$ with 4.0 mL of 98% TBP.} \\
\text{Figure 5. Chemical shift of the H$_2$O proton peak (in ppm) with} \\
&\text{respect to the molar ratio of HNO$_3$/TBP in TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$.} \\
\text{Figure 6. PNMR spectrum of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ in CDC$_3$. The} \\
&\text{complex was prepared by mixing 4 mL of TBP and 1 mL of 15.5} \\
&\text{M HNO$_3$; volume ratio of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ to CDC$_3$ = 1:1.} \\
\text{Figure 7. PNMR spectrum of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ in CDC$_3$. The} \\
&\text{complex was prepared by mixing 4 mL of TBP and 1 mL of 15.5} \\
&\text{M HNO$_3$; volume ratio of TBP($\text{HNO}_3$)$_x$(H$_2$O)$_y$ to CDC$_3$ = 1:1.} \\
\end{align*}
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complex when dissolved in a low dielectric constant solvent as a result of an antisolvent effect. The acid formation from the complex due to the antisolvent effect becomes miscible with SF-CO₂ at 14 MPa with any mole fractions. This implies that a large amount of the temperature investigated, there exists a maximum aggregated to certain sizes that would make the solution cloudy. Future experiments to evaluate nitric acid transition temperature above which the complex and aqueous solution using TBP(HNO₃)₈(H₂O)₀.₅, complex in SF-CO₂ was also evaluated by visual observation of the solution using a high-pressure view cell. Figure 8 shows the phase boundaries of the TBP(HNO₃)₈(H₂O)₀.₅ complex in SF-CO₂ at three different temperatures with respect to pressure and the mole fraction of the solute. The isothermal phase boundaries given in Figure 8 represent the transition pressures from a two-phase region into a single-phase solution for the complex with mole fractions greater than 10⁻⁴. At each temperature investigated, there exists a maximum transition temperature above which the complex and CO₂ are miscible. For example, at 323.15 K the complex becomes miscible with SF-CO₂ at 14 MPa with any mole fractions. This implies that a large amount of the complex can be dissolved in SF-CO₂ above this specific pressure for the given temperature. The maximum phase transition temperature for the complex increases with the temperature of the system varying from 11 MPa at 313.15 K to 17 MPa at 333.15 K.

A similar phase behavior was reported for the TBP–CO₂ system. The maximum transition pressure reported for the mixed TBP–CO₂ system at 323.15 K was 11 MPa, lower than that of the mixed TBP(HNO₃)₁₈(H₂O)₀.₅–CO₂ system observed in this study. A critical opalescence was also observed in our system, suggesting the presence of a pseudocritical point for the mixture. The correlated curves plotted in Figure 8 were obtained by using the same approach as that described in the literature.

Conclusions

Some properties of a CO₂-soluble Lewis base complex composed of TBP and nitric acid are described in this paper. The complex with a general formula of TBP([HNO₃]TBP) is miscible with SF-CO₂ above a certain pressure and allows dispersing of high concentrations of nitric acid in the supercritical fluid phase for chemical reactions. Chemical analysis and NMR spectroscopic data suggest that there are two types of this complex, one with a [HNO₃]/[TBP] ratio of less than 1 and the other greater than 1. When the complex was dissolved in a low dielectric constant solvent (chloroform), nitric acid was observed in the solution according to PNMR measurements. Both types of the TBP–nitric acid complex are capable of dissolving uranium dioxide and lanthanide oxides in SF-CO₂. This method of dispersing inorganic acids in SF-CO₂ for dissolution of metal oxides may have a wide range of applications for chemical processing in SF-CO₂ with minimum liquid waste generation.

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Dissolution of uranium dioxide in supercritical fluid carbon dioxide

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Uranium dioxide can be dissolved in supercritical CO2 with a CO2-phile TBP-HNO3 complexant to form a highly soluble UO2(NO3)2·2TBP complex; this new method of dissolving UO2 that requires no water or organic solvent may have important applications for reprocessing of spent nuclear fuels and for treatment of nuclear waste.

A key chemical process in the nuclear industry is the extraction and purification of uranium in the initial production of fuel for nuclear reactors and in the reprocessing of spent nuclear fuel. The most commonly used commercial process to achieve this objective is the PUREX (Plutonium Uranium Extraction) process, which involves the dissolution of spent nuclear fuel in strong nitric acid and the subsequent solvent extraction of uranium and plutonium from the acid solution using tri-n-butylphosphosphate (TBP) as an extractant. The extracted uranium and plutonium nitrate TBP complexes are further separated by chemical steps to yield pure uranium and plutonium dioxide. The PUREX process, though highly efficient, has the inherent drawbacks of generating large volumes of high level wastes accumulated from the wastes build-up program during the Cold War period (over the world). In evaluating any acceptable new techniques for reprocessing of spent nuclear fuels in the future, reduction of waste generation is an important criterion for consideration.

The possibility of using supercritical fluid carbon dioxide as a solvent for reprocessing of spent nuclear fuels was suggested recently in the literature. Supercritical CO2 is considered an excellent green solvent because it is non-toxic and environmentally benign. Carbon dioxide is also cheap, readily available in relatively pure form, and has moderate critical constants (Tc = 31.3 °C, Pc = 72.8 atm and ρc = 0.45 g cm−3). A major advantage of using supercritical CO2 for reprocessing spent nuclear fuels is the possibility of eliminating the acid and organic solvent required in the conventional PUREX process. Since the solvation strength of a supercritical fluid depends on the density of the fluid phase, selective dissolution and separation of solutes may also be possible in supercritical CO2. Rapid separation of the dissolved metal complexes can be easily achieved by reduction of the fluid pressure to cause precipitation of the solutes, and the gas can be recycled for repeated use. This approach does not directly contribute to global warming, as the CO2 used in this process is generated as a by-product of other industrial processes. A major problem for developing this new process is to identify a complexing agent that will effectively dissolve the main component of the spent nuclear fuel, basically uranium dioxide, in supercritical fluid CO2.

The hexavalent uranyl ion (UO2)2+ is known to form CO2-soluble complexes with a number of complexing agents including TBP and β-diketones. In an earlier report, we showed that uranyl ions in strong nitric acid solutions could be extracted by supercritical CO2 containing TBP. The extracted uranyl complex UO2(NO3)2·2TBP has an unusually high solubility in supercritical CO2 of the order of 4.2 × 10−1 mol L−1 at 40 °C and 200 atm. In another report, we demonstrated that uranium trioxide UO3 could be dissolved in supercritical CO2 with a fluorinated β-diketone tetraylfluoronitrosylfluorocetylacetone (Htta) and TBP forming the uranyl complex UO2(Htta)2·2TBP which has a solubility of 7.5 × 10−3 mol L−1 at 40 °C and 200 atm in supercritical CO2. This reaction, however, is not effective for dissolution of tetravalent uranium dioxide UO2. In our previous experiments regarding the extraction of uranyl ions from nitric acid solutions, we noticed that HNO3 could also be extracted by TBP forming a highly soluble complex in the supercritical CO2 phase. Our recent experiments show that this CO2-phile TBP-HNO3 complexant can oxidize UO2 to the hexavalent state leading to the formation of the highly soluble UO2(NO3)2·2TBP in supercritical CO2. This paper describes the initial results obtained from our laboratory regarding the direct dissolution of uranium dioxide is supercritical CO2 using the TBP-HNO3 complexant as an extracting agent.

TBP is known to form complexes with aqueous HNO3, and the 1:1 and 2:1 (TBP:HNO3 mole ratio) complexes are the predominating species when formed with 3 M or lower molarity nitric acid solutions. The TBP-HNO3 complexes also contain water with different hydration numbers. In this study, the TBP-HNO3 reagent was prepared by adding 5.0 mL of TBP to 0.82 mL concentrated nitric acid (69.5%, ρ = 1.42 g cm−3) in a glass tube with a stopper. This mixture of TBP and HNO3 (about 1:0.7 mole ratio) was shaken vigorously for 5 min followed by centrifuging for 20 min. After centrifugation, 3 mL of the TBP phase was removed for supercritical fluid experiments. The density of the TBP phase was measured to be 1.035 g cm−3. The remaining aqueous phase was found to have a pH about 1 after 20 times dilution in water, indicating most of the HNO3 had reacted with TBP to form the TBP–HNO3 complex. Upon addition of the TBP–HNO3 complex to CDC13, small water droplets were formed in the solution indicating the water in the complex would precipitate in the organic solution. A 300 MHz proton NMR spectrum of the TBP–HNO3 complex was taken by placing D2O in an insert separated from the complex sample in a regular NMR tube. The D2O in this case was used to lock the NMR spectrum. The NMR spectrum showed a resonance at 10.28 ppm which is attributed to HNO3 and other peaks at 4.26 ppm (dt), 1.86 ppm (qnt), 1.61 ppm (sext) and 1.14 (t) ppm for TBP. The peak areas of TBP and HNO3 species complexed with TBP. Upon addition of the TBP–HNO3 complex to CDC13, a small water droplet was formed in the solution indicating the water in the complex would precipitate in the organic solution. The 300 MHz proton NMR spectrum of the TBP–HNO3 complex was taken by placing D2O in an insert separated from the complex sample in a regular NMR tube. The D2O in this case was used to lock the NMR spectrum. The NMR spectrum showed a resonance at 10.28 ppm which is attributed to HNO3 and other peaks at 4.26 ppm (dt), 1.86 ppm (qnt), 1.61 ppm (sext) and 1.14 (t) ppm for TBP. The peak areas of TBP and HNO3 species complexed with TBP. Upon addition of the TBP–HNO3 complex to CDC13, a small water droplet was formed in the solution indicating the water in the complex would precipitate in the organic solution. The 300 MHz proton NMR spectrum of the TBP–HNO3 complex was taken by placing D2O in an insert separated from the complex sample in a regular NMR tube. The D2O in this case was used to lock the NMR spectrum. The NMR spectrum showed a resonance at 10.28 ppm which is attributed to HNO3 and other peaks at 4.26 ppm (dt), 1.86 ppm (qnt), 1.61 ppm (sext) and 1.14 (t) ppm for TBP. The peak areas of TBP and HNO3 species complexed with TBP. Upon addition of the TBP–HNO3 complex to CDC13, a small water droplet was formed in the solution indicating the water in the complex would precipitate in the organic solution.
dioxide in a powder form with size < 0.15 mm in diameter was obtained from Alfa Aesar (Ward Hill, MA). Uranium trioxide was also obtained from Alfa Aesar with a size of about 0.15–0.25 mm.

The uranium oxide dissolution experiments were performed with supercritical CO₂ containing TBP–HNO₃ flowing through the system at a rate of 0.4 mL min⁻¹ measured at the pump. The dissolved uranium complex was collected in chloroform followed by back extraction with 8 M HNO₃ and washed by deionized water twice. The combined acid-water solution was analyzed by spectrophotometric method۪ and by ICP-AES for uranium determination. UV–VIS spectroscopy showed that the trapped uranium complex had an identical absorption spectrum to that reported for UO₂(NO₃)₂-2TBP.⁵ Fig. 1 shows the dissolution of UO₂ and UO₃ in supercritical CO₂ with the TBP–HNO₃ complexant at 60 °C and 150 atm (ρ = 0.613 g cm⁻³). The results are expressed as the cumulative mass of uranium (in mg) found in the collection solution with time. The amount of the TBP–HNO₃ complexant dissolved in the CO₂ phase during the dynamic extraction process was determined by measuring the volume change of the complexant before and after the experiment. The amount of the TBP–HNO₃ complexant at different densities (g cm⁻³) was 0.766 (60 °C, 150 atm), 0.94 (65 °C, 250 atm), 1.10 (60 °C, 200 atm), 1.61 (60 °C, 150 atm), 1.78 (60 °C, 110 atm).

Direct dissolution of uranium dioxide in supercritical CO₂ under the specified conditions apparently occurred rapidly. Dissolution of UO₂ in supercritical CO₂ under the same conditions was more effective than that of UO₃. This is expected because UO₂ is in the hexavalent oxidation state which is ready to form the CO₂ soluble UO₂(NO₃)₂-2TBP complex. The dissolution of UO₂ may be represented by eqn. (1) assuming the TBP–HNO₃ complex has a 1:1 stoichiometry:

\[
\text{UO}_2(\text{solid}) + 8/3 \text{ TBP–HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_{2/3} \cdot \text{2TBP} + 2/3 \text{ NO} + 4/3 \text{H}_2\text{O} + 2/3 \text{ TBP} \quad (1)
\]

Similar equations can be written for the 2:1 and other TBP–HNO₃ complexes with different stoichiometry.

Dissolution of UO₂ in liquid CO₂ was slow relative to that observed in the supercritical CO₂ experiments (Fig. 2). Because oxidation of UO₂ was required in the dissolution process, diffusion of the oxidized products in the liquid phase could be a factor limiting the dissolution rate. The diffusion coefficient of supercritical CO₂ is typically an order of magnitude higher than that of the liquid. Under the same liquid CO₂ conditions, dissolution of UO₂ was about the same as that in the supercritical phase perhaps because oxidation was not required in this case.

The density of supercritical CO₂ is known to influence the solvation strength and hence solubility of solutes in the supercritical fluid phases. The dissolution of UO₂ in supercritical CO₂ increased rapidly with the density of the fluid phase as shown in Fig. 3. The amount of UO₂ dissolved in the supercritical CO₂ phase at density 0.7662 g cm⁻³ was about an order of magnitude higher that at density 0.6125 g cm⁻³ after 12 minutes of dynamic extraction. The density effect could be partly due to the increased amount of the TBP–HNO₃ complexant dissolved in the CO₂ phase during the dynamic extraction process was determined by measuring the volume change of the complexant before and after the experiment. The amount of the TBP–HNO₃ complexant at 60 °C and 150 atm (ρ = 0.613 g cm⁻³) was 0.766 (60 °C, 250 atm), 0.94 (65 °C, 200 atm), 1.10 (60 °C, 150 atm), 1.61 (60 °C, 110 atm).

Notes and references