DOE-EMSP Project Annual Report

Project Title: Solvent Effects on Metal Complexation with Crown Ethers from Liquid
to Supercritical Fluids (DE-FG07-98ER 14913)

Principle Investigator: C.M. Wai, Department of Chemistry, University of Idaho,
Moscow, Idaho 83844 Chien M. Wai

Reporting Date: November 25, 2002

Introduction

The purpose of this project is to study the salvation effects of metal-crown ether complexation in different solvents. It has been suggested in the literature that supercritical fluid carbon dioxide (SF-CO_2) is a tunable solvent because its salvation environment can be varied with the fluid density. In this project, spectroscopic techniques including nuclear magnetic resonance (NMR) and Fourier Transform Infrared (FTIR) were used to evaluate salvation effects of metal crown complexation in organic solvents and in SF-CO_2. In most solvent extraction systems, water is often involved in the extraction processes. We have carried out extensive studies of water-crown ether interactions in different solvents and in SF-CO_2 using NMR and FTIR techniques. Water molecules can be attached to crown ethers through hydrogen bonding of H-O-H to the oxygen atoms of crown ether cavities. This type of interaction is like a Lewis acd-Lewis base complexation. During the course of this project, we noticed that some CO_2-soluble Lewis base such as tri-n-butyl-phosphate (TBP) can also form such Lewis acid-Lewis base complexes with water and other inorganic acids including nitric acid and hydrochloric acid. Inorganic acids (e.g. nitric acid) are normally not soluble in SF-CO_2. However, because TBP is highly soluble in SF-CO_2, an inorganic acid bound to TBP via hydrogen bonding becomes CO_2-soluble. This Lewis acid-Lewis base complex approach provides a method of introducing inorganic acids into supercritical fluid CO_2 for chemical reactions.

One successful example is the direct dissolution of solid uranium dioxide in supercritical CO_2 using a CO_2-soluble TBP-nitric acid complex. This dissolution process probably involves the oxidation of UO_2 solid to $UO_2(NO_3)_2$ followed by formation of $UO_2(NO_3)_2 \cdot 2TBP$ which is soluble in supercritical CO_2. This dry supercritical fluid CO2 dissolution of uranium dioxide appears to have a wide range of applications for the nuclear industry including reprocessing of spent nuclear fuel and treatment of nuclear wastes. Our result of uranium dioxide dissolution in supercritical carbon dioxide using a CO2-soluble TBP-nitric acid complex was published last year in *Chemical Communications*. It was cited by *Chemical and Engineering News* (C&E News) in the October 1, 2001 issue and also reported by *New Scientist* on June 8, 2003. We are currently characterizing the TBP-nitric acid complex using different methods.

In this annual report, the following published papers and manuscripts derived from the DOE-EMSP project are attached. The support of DOE-EMSP program is acknowledged in these papers and manuscripts.

1. Dissolution of uranium dioxide in supercritical fluid carbon dioxide. Published in Chemical Communications, 2001, p 1869-1869. A news report appeared on October 1, 2001 issue of C&E News regarding the significance of this paper is also attached.
2. Ultrasound enhaenment of dissolution kinetics of uranium oxides in supercritical carbon dioxide. Published in *Journal of Chemical Technology and Biotechnology*, 2001, Vol. 76, p 1223-1226.
3. Determination of partition coefficients of crwon ethers between water and organic solvents by proton nuclear magnetic resonance. A manuscript in preparation for journal submission.
4. Characterization of $TBP-HNO_3-H_2O$ complex-a new extractant for direct dissolution of UO_2 in supercritical CO_2. A manuscript in preparation for journal submission.

4. An FTIR study of crown ether complexation with water in liquid and supercritical carbon dioxide. A manuscript in preparation for journal submission.

A final report for this DOE-EMSP project is currently in preparation. The final project report will be submitted to your office by the end of 2002.

CHEMCOMM
Communication
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Dissolution of uranium dioxide in supercritical fluid carbon dioxide

M. D. Samsonov,[a] **C. M. Wai,***[a] **Su-Chen Lee,**[a] **Yuri Kulyako**[b] **and N. G. Smart**[c]

[a] *Department of Chemistry, University of Idaho, Moscow, Idaho 83844, USA*
[b] *Laboratory of Radiochemistry, Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 117975 Moscow, Russia*
[c] *Chemical Process Group, BNFL, Sellafield, Cumbria, UK CA20 1PG*

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Uranium dioxide can be dissolved in supercritical CO_2 with a CO_2-philic TBP–HNO_3 complexant to form a highly soluble $UO_2(NO_3)_2 \cdot 2TBP$ complex; this new method of dissolving UO_2 that requires no water or organic solvent may have important applications for reprocessing of spent nuclear fuels and for treatment of nuclear wastes.

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*-butylphosphate (TBP) as an extractant.[1,2] 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 liquid–liquid extraction including generation of aqueous and organic liquid wastes. The large volumes of high level wastes accumulated from the weapons build-up program during the Cold War period are one example of the nuclear waste problems facing the USA.[3] Spent fuels from commercial nuclear power plants are still reprocessed today using the Purex process to recover unused uranium for recycling by several countries excluding the USA. Developing techniques for effective treatment of the wastes generated in the past and for reprocessing of spent nuclear fuels in the future has been one of the most actively pursued research areas by nuclear scientists all 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.[4] Supercritical CO_2 is considered a 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 (T_c = 31.3 °C, P_c = 72.8 atm and ρ_c = 0.45 g cm^{-3}). A major advantage of using supercritical CO_2 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 CO_2. 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 CO_2 used in this process is generated as a by-product from other chemical 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 CO_2.

The hexavalent uranyl ion $(UO_2)^{2+}$ is known to form CO_2-soluble complexes with a number of complexing agents including TBP and β-diketones.[5] In an earlier report, we showed that uranyl ions in strong nitric acid solutions could be extracted by supercritical CO_2 containing TBP.[6] The extracted uranyl complex $UO_2(NO_3)_2 \cdot 2TBP$ has an unusually high solubility in supercritical CO_2, of the order of 4.2×10^{-1} mol L^{-1} at 40 °C and 200 atm.[7] In another report, we demonstrated that uranium trioxide UO_3 could be dissolved in supercritical CO_2 with a fluorinated β-diketone thenoyltrifluoroacetylacetone (Htta) and TBP forming the uranyl complex $UO_2(tta)_2 \cdot 2TBP$ which has a solubility of 7.5×10^{-3} mol L^{-1} at 40 °C and 200 atm in supercritical CO_2.[8] This reaction, however, is not effective for dissolution of tetravalent uranium dioxide UO_2. In our previous experiments regarding the extraction of uranyl ions from nitric acid solutions, we noticed that HNO_3 could also be extracted by TBP forming a highly soluble complex in the supercritical CO_2 phase.[9] Our recent experiments show that this CO_2-philic TBP–HNO_3 complexant can oxidize UO_2 to the hexavalent state leading to the formation of the highly soluble $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2. This paper describes the initial results obtained from our laboratory regarding the direct dissolution of uranium dioxide in supercritical CO_2 using the TBP–HNO_3 complexant as an extracting agent.

TBP is known to form complexes with aqueous HNO_3, and the 1:1 and 2:1 (TBP:HNO_3 mole ratio) complexes are the predominating species when formed with 3 M or lower molarity nitric acid solutions.[10] The TBP–HNO_3 complexes also contain water with different hydration numbers.[10] In this study, the TBP–HNO_3 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 HNO_3 (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 HNO_3 had reacted with TBP to form the TBP–HNO_3 complex. Upon addition of the TBP–HNO_3 complex to $CDCl_3$, 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–HNO_3 complex was taken by placing D_2O in an insert separated from the complex sample in a regular NMR tube. The D_2O in this case was used to lock the NMR spectrum. The NMR spectrum showed a resonance peak at 10.28 ppm which is attributed to HNO_3 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 HNO_3 indicated a proton ratio close to 27:2 for the TBP–HNO_3 complex. The HNO_3 proton NMR peak suggests a hydrated HNO_3 species complexed with TBP. The solubility of this TBP–HNO_3 complex in liquid CO_2 at room temperature and 80 atm is about 0.38 mL/mL CO_2. The TBP–HNO_3 complex (about 3 mL) was placed in a 10.4 mL stainless steel cell which was connected upstream to a 3.47 mL extraction cell containing about 40–60 mg of a uranium oxide. Liquid CO_2 was added to the cells using an ISCO model 260D syringe pump and the system was heated in an oven at a desired temperature. Uranium

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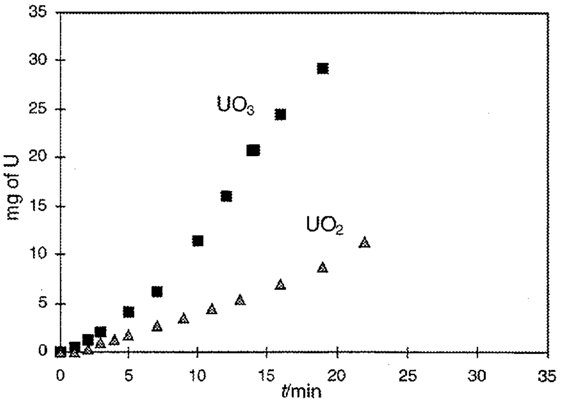

Fig. 1 Cumulative mass of uranium extracted from UO_3 and UO_2 with time by supercritical CO_2 containing the TBP–HNO_3 extractant (60 °C, 150 atm, flow rate = 0.4 mL min^{-1}).

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 CO_2 containing TBP–HNO_3 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 HNO_3 and washed by deionized water twice. The combined acid-water solution was analyzed by spectrophotometric method[11] 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 $UO_2(NO_3)_2 \cdot 2TBP$.[7] Fig. 1 shows the dissolution of UO_2 and UO_3 in supercritical CO_2 with the TBP–HNO_3 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–HNO_3 complexant dissolved in the CO_2 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–HNO_3 complexant in the supercritical CO_2 stream was determined to be about 0.08 mL/mL of CO_2 at 60 °C and 150 atm. The amount of the TBP–HNO_3 complexant was in excess with respect to UO_2 in our dynamic extraction experiments. Direct dissolution of UO_2 in supercritical CO_2 under the specified conditions apparently occurred rapidly. Dissolution of UO_3 in supercritical CO_2 under the same conditions was more effective than that of UO_2. This is expected because UO_3 is in the hexavalent oxidation state which is ready to form the CO_2 soluble $UO_2(NO_3)_2 \cdot 2TBP$ complex. The dissolution of UO_2 may be represented by eqn. (1) assuming the TBP–HNO_3 complex has a 1:1 stoichiometry:

$$UO_2(\text{solid}) + 8/3\ \text{TBP–}HNO_3 \rightarrow UO_2(NO_3)_2 \cdot 2TBP + 2/3\ NO + 4/3\ H_2O + 2/3\ \text{TBP} \qquad (1)$$

Similar equations can be written for the 2:1 and other TBP–HNO_3 complexes with different stoichiometry.

Dissolution of UO_2 in liquid CO_2 was slow relative to that observed in the supercritical CO_2 experiments (Fig. 2). Because oxidation of UO_2 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 CO_2 is typically an order of magnitude higher than that of the liquid. Under the same liquid CO_2 conditions, dissolution of UO_3 was about the same as that in the supercritical phase perhaps because oxidation was not required in this case.

The density of supercritical CO_2 is known to influence the solvation strength and hence solubility of solutes in the supercritical fluid phases. The dissolution of UO_2 in supercritical CO_2 increased rapidly with the density of the fluid phase as shown in Fig. 3. The amount of UO_2 dissolved in the supercritical CO_2 phase at density 0.7662 g cm^{-3} was about an order of magnitude higher than 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–HNO_3 complex in the supercritical CO_2 stream caused by the increase in density of the fluid phase. This strong dependence of UO_2 dissolution on supercritical CO_2 density may be used as a parameter for selective dissolution and separation of UO_2 in supercritical CO_2. The direct dissolution of uranium dioxide demonstrated in this study suggests a possibility of dissolving spent nuclear fuels in supercritical CO_2 without the use of conventional acid and organic solvents. This new technique could offer many benefits for the 21st century nuclear industry including reduction in waste generation and improved efficiency of chemical processing.

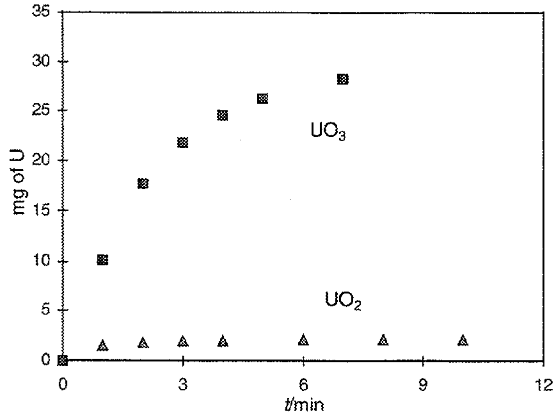

Fig. 2 Cumulative mass of uranium extracted from UO_3 and UO_2 in liquid CO_2 containing the TBP–HNO_3 extractant (21 °C, 80 atm, flow rate = 0.4 mL min^{-1}).

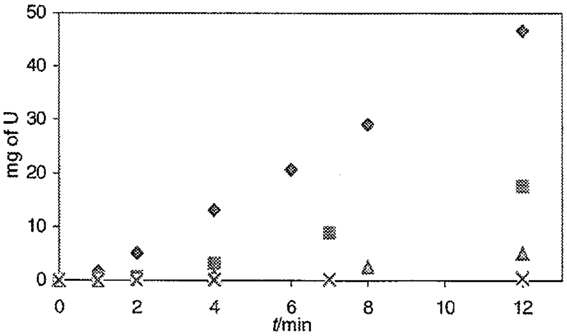

Fig. 3 Cumulative mass of uranium extracted from UO_2 by supercritical CO_2 with the aid of the TBP–HNO_3 complexant at different densities (g cm^{-3}). (◆) 0.766 (65 °C, 250 atm), (▨) 0.732 (60 °C, 200 atm), (△) 0.613 (60 °C, 150 atm), (×) 0.378 (60 °C, 110 atm).

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Notes and references

1 G. T. Seaborg, *The Actinide Elements*, McGraw-Hill, Inc., New York, 1954, pp. 273–284.
2 A. Schneider and B. G. Wahling, *Actinide Separations*, ACS Symposium Series 117, ACS, Washington, D.C., 1980, pp. 279–290.
3 U.S. Office of the Assistant Secretary for Nuclear Energy, Washington D.C., Dept. of Energy, 1979 (DOE/EIS-0023).
4 N. G. Smart, C. L. Phelps and C. M. Wai, *Chem. Br.*, 1998, **34(8)**, 34.
5 C. M. Wai and S. Wang, *J. Chromatogr. A.*, 1997, **785**, 369.
6 Y. Lin, N. G. Smart and C. M. Wai, *Environ. Sci. Technol.*, 1995, **29**, 2706.
7 M. J. Carrott, B. E. Waller, N. G. Smart and C. M. Wai, *Chem. Commun.*, 1998, 373.
8 M. J. Carrott and C. M. Wai, *Anal. Chem.*, 1998, **70**, 2421.
9 C. M. Wai, Y. Lin, M. Ji, K. L. Toews and N. G. Smart, *Progress in Metal Ion Separation and Preconcentration*, ACS Symposium Series 716, ACS, Washington, D.C., 1999, ch. 23, p. 390.
10 H. Naganawa and S. Tachimori, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 809.
11 J. S. Fritz and M. Jonson-Richard, *Anal. Chim. Acta.*, 1959, **20**, 164.

Oct. 2001

TRAGEDY

FERTILIZER PLANT EXPLODES IN FRANCE

Blast at TotalFinaElf's ammonium nitrate facility kills at least 29 people

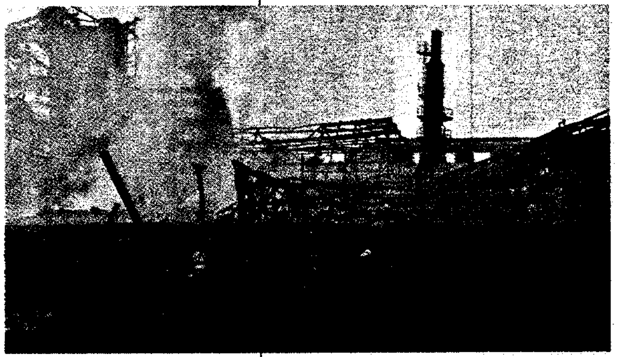
A HUGE EXPLOSION ROCKED the industrial French city of Toulouse on Sept. 21 when a fertilizer plant operated by Grande Paroisse—a subsidiary of Atofina, the chemical arm of TotalFinaElf—blew up. Its cause is not known, but available information strongly suggests it was accidental.

The official death toll stood at 29. Of the roughly 650 people hospitalized, 34 were judged to be gravely injured.

The blast not only demolished the Grande Paroisse plant, which employs 460, but also destroyed neighboring buildings and blew out half the window glass in the city of 1 million, according to local reports. Damage was also extensive at the SNPE rocket-fuel and chemical plant, a major phosgene producer located across the Garonne River from the Grand Paroisse plant. A cloud of chemical products, mainly ammonia, blanketed the city, but it was not considered toxic since it was diluted in the atmosphere.

Grande Paroisse produces nitrogen fertilizers marketed under the name AZF, as well as chemical intermediates. The culprit suspected in the blast, ammonium nitrate, is well known for its explosive potential. In one famous incident in 1947, a ship loaded with ammonium nitrate exploded in the Texas City harbor, destroying the harbor and adjacent industrial facilities and killing at least 600 people. More recently, ammonium nitrate was used in the 1995 bombing of the Alfred P. Murrah federal office building in Oklahoma City.

In addition to government investigations, TotalFinaElf has appointed its own internal commission to uncover the cause of the explosion.—KAREN WATKINS



AP PHOTO

SHATTERED Twisted, smoldering wreckage covers the site of fertilizer plant that exploded on Sept. 21 near Toulouse, France.

SCIENCE

SPENT NUCLEAR FUEL REPROCESSED IN CO_2

Supercritical separation may reduce volume of highly radioactive waste

SUPERCRITICAL FLUID CARbon dioxide could find important applications in spent nuclear fuel reprocessing and nuclear waste treatment, according to an international team of scientists.

The research team showed that solid uranium dioxide, a nuclear fuel, dissolves in supercritical CO_2 containing a complex of tri-*n*-butylphosphate (TBP) and nitric acid. The resulting uranyl nitrate-TBP complex is recovered by reducing the fluid pressure to atmospheric pressure and then allowing the gas to expand into a collection vial.

The work was carried out by scientists at the University of Idaho, Moscow; the Vernadsky Institute of Geochemistry & Analytical Chemistry, Moscow, Russia; and British Nuclear Fuels Ltd. (BNFL), Sellafield, England [*Chem. Commun.*, 2001, 1868].

"The extractant oxidizes uranium(IV) to uranium(VI) to form a complex that is very soluble in supercritical CO_2," explains Idaho chemistry professor Chien M. Wai. "This process does not require any aqueous solution or organic solvent to dissolve the UO_2.

"Dissolution of UO_2 in supercritical CO_2 minimizes waste generation," Wai continues. "The new extraction method can also be used for decontamination of actinide-contaminated solid wastes that conventionally require acid or aqueous solution leaching to remove the contaminants from solid matrices."

The report is significant, says William R. Pitner, a research chemist at Queen's University of Belfast, Northern Ireland, who carries out work on nuclear fuel reprocessing. "It demonstrates the applicability of an alternative technology to the nuclear industry," he says. "As an industry which will continue to evolve in the decades to come, it is important that it continue to investigate nontraditional methods that may complement or replace existing processes," Pitner adds.—MICHAEL FREEMANTLE

IN BRIEF: FAR OUT FLYBY

It may not look like much, but this closest ever look, obtained on Sept. 22, at the icy, rocky nucleus of a comet has space scientists excited. The 5-mile-long nucleus of the 10-mile-long comet Borrelly has a number of unexpected features, including dark patches that appear to be higher than surrounding terrain.

COURTESY OF NASA

New Scientist
June 8, 2002

Peter Marlow/Magnum

Hot stuff

Could a new technique make the reprocessing of spent nuclear fuel less hazardous?

WHAT to do with spent fuel is one of the nuclear industry's big headaches. Reprocessing is risky, expensive and controversial, generating massive quantities of liquid radioactive waste that threatens the environment. Yet simply discarding spent fuel is very wasteful. Now a new reprocessing technique could dramatically cut the volumes of nuclear waste

Nuclear fuel rods have to be replaced every few years because fission products such as strontium build up inside them. At levels of just 5 to 10 per cent, these waste products block neutrons and significantly reduce the efficiency of the fission reaction. Some countries, including the US and Germany, simply store their used fuel rods, but others, including Britain, reprocess the spent rods to extract the unused uranium and plutonium.

Conventional reprocessing plants dissolve spent fuel in nitric acid and then remove the uranium, leaving large quantities of liquid radioactive waste. This is dried, converted to glass or "vitrified", and then sent for storage. The risk of contamination when dealing with these huge amounts of radioactive liquid is one reason why environmentalists oppose reprocessing.

Now, a group of researchers led by Chen Wai, a chemist at the University of Idaho, has developed an alternative technique that generates only one-hundredth as much waste and costs two-thirds as much as conventional reprocessing. Instead of dissolving fuel in nitric acid, the team uses carbon dioxide at such a high temperature and pressure that it becomes "supercritical". Supercritical fluids hover between being a gas and a liquid, with some of the properties of each.

The key to the process is a complex that forms between the unused uranium dioxide fuel and a chemical based on a solvent called tributyl phosphate (TBP). This complex dissolves in the supercritical carbon dioxide. The same goes for plutonium dioxide, which is sometimes used as a fuel mixed in with the uranium. The fission products that gum up the fuel rods don't react with the TBP compound, and get left behind when the uranium-TBP and plutonium-TBP dissolve in the CO_2. This creates a relatively small volume of fission-product waste compared with conventional reprocessing, and it can be filtered out. What's more, uranium oxide needs only a small volume of supercritical CO_2 to dissolve, compared with the amount of nitric acid that would be needed in conventional reprocessing.

The solution containing uranium and plutonium is transferred to a second vessel, where the pressure is lowered. This allows the CO_2 to evaporate, leaving behind the uranium-TBP and plutonium-TBP. There's no huge volume of radioactive liquid left sloshing around, and the uranium dioxide and plutonium dioxide can then be liberated from the TBP complex, though Wai is not saying how they do this.

Wai says the pressures needed to operate a supercritical reprocessing plant are no higher than those commonly used in nuclear reactors. The plant would be able to recycle most of its CO_2, and any gas that was vented could be filtered to remove radioactive particles. Wai and collaborator Youichi Enokida at Nagoya University in Japan have also found that blasting the uranium with ultrasound makes it dissolve 10 times faster. The Japanese government has just set aside $4 million for a project designed to assess the commercial viability of the new process.

Jim Riccio, a nuclear policy analyst with Greenpeace in Washington DC, says that while a reduction in the amount of reprocessing waste would be an obvious improvement, he would prefer to see nuclear energy phased out altogether and replaced with renewable sources such as solar power. He also points out that, like conventional reprocessing, the CO_2 technique isolates plutonium that can be used to make nuclear weapons. **Mark Schrope**

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Ultrasound enhancement of dissolution kinetics of uranium oxides in supercritical carbon dioxide

TI Trofimov,[1,2] MD Samsonov,[1,2] SC Lee,[1] NG Smart[3] and CM Wai[1]*

[1] *Department of Chemistry, University of Idaho, Moscow, ID, 83844, USA*
[2] *Laboratory of Radiochemistry, VI Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow, Russia*
[3] *Research and Technology, BNFL, Sellafield, Cumbria CA20 1PG, UK*

Abstract: The enhanced dissolution of uranium oxides by the application of ultrasound in supercritical fluid carbon dioxide containing dissolved 4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and tributyl phosphate is demonstrated. Under conditions of 60 °C and 150 atm the steady state dissolution of UO_3 with sonification is increased by approximately 100%. Furthermore, the effect of adding hydrogen peroxide to the supercritical system above enables the lower oxides of uranium, UO_2 and U_3O_8, to be extracted.

Keywords: uranium oxides; supercritical fluid carbon dioxide; ultrasound; dissolution kinetics

INTRODUCTION

The extraction and purification of uranium is a key chemical process in the nuclear industry both in the initial production of fuel for nuclear reactors and in the reprocessing of spent nuclear fuel. By far the most commonly used process involves the dissolution of impure uranium materials in strong nitric acid solutions and the subsequent purification of these solutions using a solvent extraction process, utilizing tributyl phosphate (TBP) as the active extractive reagent.[1] This is further followed by a chemical conversion step(s) into a purified solid uranium oxide material. This process is commercially referred to as the Purex process. A considerable amount of investigation has been carried out looking at alternative means of processing uranium into its pure form, including electrorefining in molten salts, distillation techniques by formation of volatile uranium fluorides and more recently utilizing supercritical fluid (SF) technology.[2,3]

The key to purification of metals in the SF phase lies in the requirement to both neutralize the charge on the metal species and create a complex which is polarity-compatible with the SF solvent.[3] Fluorinated ligands have been shown to fulfil both of these criteria.[4] Solubility studies have shown that increasing the fluorine substituents on a ligand increases the solubility of both the ligands and the metal complexes formed with the ligand in SF carbon dioxide (SF CO_2).[4,5] In terms of enhancement of a process for uranium purification there is the additional problem that the initial form of the uranium is usually in an oxide form and hence requires conversion of the oxide into a metal complex form prior to any potential processing in the SF CO_2. It has been demonstrated elsewhere that certain uranium oxides can be converted to metal complexes by direct reaction with acidic ligands in SF CO_2 and that the metal complexes formed can be transported in the SF CO_2 phase.[6] The favored acidic ligands studied thus far are from the β-diketone family, with 4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (HTTA) being widely used. While this process offers potential, the reaction kinetics of the oxides have been shown to be rather slow. In this communication we report the enhanced dissolution of uranium oxides by the application of ultrasound to the SF CO_2 reaction system.

EXPERIMENTAL

The uranium oxides included depleted UO_3 (Alfa AESAR, Ward Hill, MA, 99.8%), UO_2 (Alfa AESAR, 99.8%), and U_3O_8 (NBS Standard Reference Material). The ligands HTTA and TBP were obtained from Alfa AESAR and used without further purification. SFE grade carbon dioxide (Air Products, Allentown, PA) was used for all extractions. Extracted products were collected in a trap solution (ACS-grade

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* Correspondence to: CM Wai, Department of Chemistry, University of Idaho, Moscow, ID, 83844, USA

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trichloromethane obtained from Fisher, Fairlawn, NJ) through the restrictors made from 150 mm lengths of deactivated fused silica, 50 µm id, purchased from Polymicro Technologies (Phoenix, AZ). Uranium was back extracted from the trap solutions using 50% nitric acid (Fisher, Fairlawn, NJ) followed by washing of the organic phase with deionized water produced by a Milli-Q Ultra-pure water system (Millipore Inc).

An ISCO model 260D syringe pump (Isco, Inc, Lincoln, NE) with a Series D controller was used to deliver CO_2 to the extraction system. The experimental system used is illustrated in Fig 1. Standard $10.4\,cm^3$ and $3.47\,cm^3$ stainless steel HPLC cells (Keystone scientific Inc, PA) were used as ligand and extraction cells, respectively. The ligand cell containing HTTA was placed upstream from the extraction cell containing a uranium oxide sample. They were put into an oven for heating the system up to the experimental temperature. TBP was injected to the system through a T-end joint using an HPLC pump, A-30 ks-pk (Eldex Lab Inc, CA, USA). This gave a constant TBP concentration of $0.18\,mol\,dm^{-3}$. The arrangement allowed extractions to be conducted statically, dynamically or using a combination of both methods (the static mode followed by dynamic one). Flow rates of CO_2 from the system were maintained at ~ 0.4–$0.5\,cm^3\,min^{-1}$. The extractions were carried out at 60 °C and 150 atm. These conditions have been found previously to be optimal for the system involved (UO_3–TTA–TBP).[6] An ultrasonic cleaner with a heater, model FS30 (Fisher Scientific, PA), was used to increase the uranium oxide dissolution. The extraction cell was placed vertically into the ultrasonic cleaner's tank with water preheated to the required temperature. The ultrasonic cleaner (USC) uses transducers mounted to the bottom of its tank to create high frequency sound waves in the tank's liquid. The output frequency of the ultrasonic device was in the range 44–48 kHz. The spectrophotometric method of uranium determination with Arsenazo I was used for analyzing the samples collected for uranium content.[7] Absorption spectra were recorded using a Cary 1E UV-Visible recording spectrophotometer.

RESULTS AND DISCUSSION

The solubility of HTTA in SC-CO_2 was measured at 60 °C and 150 atm; it was found to be 0.041 ± 0.004 M. In our studies, the SF CO_2 was saturated with HTTA by passing the SF CO_2 through a pre-saturation cell containing an excess of HTTA. Under the conditions of the experiment, the HTTA (mp 42 °C) is in the liquid state in the pre-saturation cell.

Reaction of UO_3 in SF CO_2

In preliminary experiments the direct reaction of UO_3 with HTTA in large excess was observed to occur with high efficiency in a static reaction cell system.[6] Although high conversion efficiency to $UO_2(TTA)_2.H_2O$ was observed, low transport of the complex from the cell in SF CO_2 was also observed. Instead the complex remained in the reaction cell as a powdery orange-colored complex. Furthermore, it was found necessary to add TBP to the extraction system to enable transport of the U from the reaction system. It is known that TBP is a stronger Lewis base than H_2O and it can replace the coordinated H_2O molecule to form the adduct $UO_2(TTA)_2.TBP$, which is quite soluble in SF CO_2.

The effect of the application of ultrasound to the dissolution of UO_3 in a SF CO_2 stream modified with TBP and HTTA is illustrated in Fig 2. The reaction conditions are 60 °C and 150 atm with an SF CO_2 stream modified with 0.041 M HTTA and 0.18 M TBP. In the absence of ultrasound the dissolution rate is found to be slow, ie the amount of U complexed and transported from the extraction cell is small. Even with the application of static time to allow the $UO_2(TTA)_2.H_2O$ complex to form, the dissolution rate is small. Confirmation that the U transported is collected, is illustrated in Table 1, where the mass balance for U in the system is presented. After

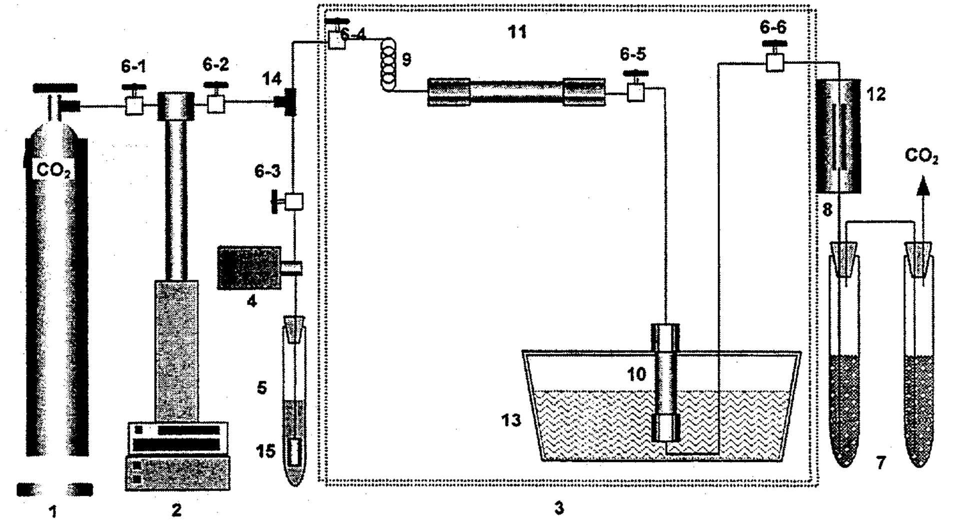

Figure 1. Schematic diagram of the experimental system for dissolution of uranium oxides in supercritical carbon doxide. 1, CO_2 cylinder; 2, syringe pump; 3, oven; 4, HPLC pump; 5, test-tube with TBP; 6-1–6-6, volumeless valves; 7, collection system; 8, restrictor; 9, fluid preheating coil; 10, extraction vessel; 11, ligand cell; 12, restrictor heater; 13, ultrasonic cleaner; 14, T-joint; 15, filter.

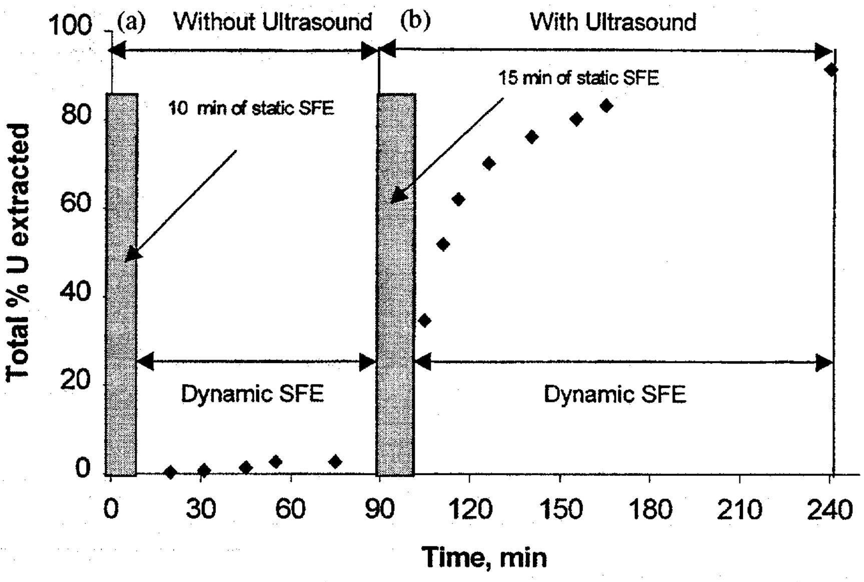

Figure 2. UO_3 dissolution in supercritical CO_2 containing TTA and TBP with and without the application of ultrasound. SFE conditions: T=60°C; P=150 atm; amount of reagents: UO_3=18.8 mg (15.6 mg of U); TTA 0.041 M and TBP 0.18 M. SFE modes: (a) 10 min of static SFE followed by dynamic one without ultrasonic cleaner; (b) 15 min of static SFE followed by dynamic one with ultrasonic cleaner.

application of the ultrasound, the dissolution rate is observed to increase greatly. This is followed by a decrease in the dissolution rate as the HTTA in the extraction system becomes depleted. The various steps involved in the dissolution reaction are outlined below:

(1) Mass transport of HTTA and TBP in SF CO_2 to UO_3 reaction site
(2) $UO_{3(s)} + 2HTTA_{(SF)} \rightarrow UO_2(TTA)_2.H_2O_{(s)}$
(3) $UO_2(TTA)_2.H_2O_{(s)} + TBP_{(SF)} \rightarrow UO_2(TTA)_2.TBP_{(s)} + H_2O_{(SF)}$
(4) $UO_2(TTA)_2.TBP_{(s)} + SF\ CO_2 \rightarrow UO_2(TTA)_2.TBP_{(SF)}$
(5) Mass transport of $UO_2(TTA)_2.TBP_{(SF)}$ in SF CO_2 from extraction cell

The dissolution of UO_3 in the presence of a continuous flow of HTTA is illustrated in Fig 3. The dissolution of the oxide and transportation in SF CO_2 is greatly enhanced by the application of the ultrasound. Both curves show a slight initiation period, which is characteristic of oxide dissolution in aqueous systems.[8] This initiation period can be defined as the time required for initiating the formation of the uranyl TTA complex. A region in which the dissolution is linear with time follows this initiation period. Such a linear region is potentially a characteristic of a solubility-limited process.[9] In unmodified SF CO_2 the solubility of $UO_2(TTA)_2H_2O$ has been reported as approximately 7×10^{-5} M,[10] while the solubility of $UO_2(TTA)_2.TBP$ in unmodified SF CO_2 is reported to be 4×10^{-3} M.[10] In the HTTA/TBP-modified SF CO_2 the actual solubility of the complex is expected to be greater than the value reported for the unmodified system. Therefore, we can reject the hypothesis that the extraction profile is a solubility-limited profile, since the complex solubility in the SF system is much greater than the actual amounts of U transported.

Table 1. Mass balance for the collection of U from the extraction system illustrated in Fig 1

	Amount of U found (mg)	
Amount of U taken (mg)	*In trap solution*	*In cell wash*
15.6 (100%)	14.8 (91.7%)	0.8 (5.5%)
	15.2 (97.2%)	

From the above discussion we conclude that step (2) is the rate limiting step, since the extraction requires the presence of HTTA in the extraction system and the amounts of U extracted are below the solubility limits of the $UO_2(TTA)_2.TBP$ in the SF CO_2 system. The rate at which the $UO_2(TTA)_2.TBP$ complex forms from the $UO_2(TTA)_2H_2O$ complex is thought to be fast in this system, since preliminary work found the displacement of water from the $UO_2(TTA)_2H_2O$ complex to be very rapid with a range of Lewis base systems.[10] The effect of the ultrasound can be attributed to cleaning the oxide surface by removing the complex formed and allowing the reaction with TTA to take place more effectively.

The reactions of UO_2 and U_3O_8 in SF CO_2

The reaction of UO_2 and U_3O_8 in SF CO_2 under conditions similar to those described above was found to be very slow. The results obtained with the

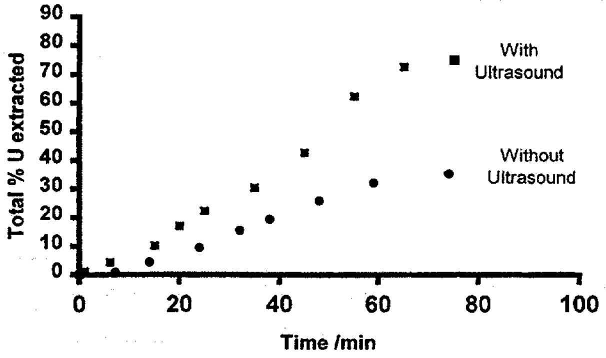

Figure 3. Dynamic SFE of UO_3 with and without the effects of ultrasound. Experimental conditions, T=60°C; P=150 atm. Flow rate, 0.5 cm^3 min^{-1}.

Table 2. Dissolution of uranium oxides in supercritical CO_2 containing TTA and TBP, in the presence of ultrasonic excitation

	Amount of reagent taken						Amount of U found in a trap solution	
	Uranium oxide (U)		HTTA		TBP			
	mg	mmole	mg	mmole	cm^3	mmole	mg	%
UO_2	27.1 (23.9)	0.09	503.7	2.27	1.0	3.68	1.19	5.0
U_3O_8	36.4 (30.9)	0.09	643.7	2.90	1.5	5.51	0.65	2.1

SFE conditions: T = 60 °C; P = 150 atm; 20 min of static SFE followed by 150 min of dynamic SFE.

Table 3. Dissolution of uranium dioxide preliminarily oxidized with H_2O_2 in 'one system' in supercritical CO_2 containing TTA and TBP using ultrasonic device

	Amount of reagent taken						Amount of U found in			
	Uranium dioxide (U)		HTTA		TBP		Trap solution		Cell wash	
	mg	mmol	mg	mmole	cm^3	mmol	mg	%	mg	%
1	22.6 (20.0)	0.08	200.0	0.90	2.7	9.94	8.5	42.6	3.7	18.5
2	16.2 (14.3)	0.06	136.3	0.61	2.6	9.60	5.2	36.1	7.7	54.1

SFE conditions: P = 150 atm; T = 60 °C; 25 min of static SFE followed by 110 min of dynamic SFE; 0.2 cm^3 of H_2O_2 were introduced into the extraction vessel followed by its heating at 90 °C for aqueous phase evaporation before SFE. The experiments were conducted in the so-called 'one system'.

application of ultrasound are illustrated in Table 2. Only a small amount of the oxide is observed to react under the specified experimental conditions. This low reaction rate is thought to be due to the stable nature of these particular uranium oxides. Since the higher oxidation state of uranium was found to be very reactive, H_2O_2 was added to the system with the aim of oxidizing the uranium to the U^{6+} state. The H_2O_2 was added to the system in the presence of the complexants and the SF CO_2. The results obtained are illustrated in Table 3. It was observed that a much greater amount of U is extracted when the oxidizing agent is added.

SUMMARY

This study has demonstrated that the formation of $UO_2(TTA)_2H_2O$ is likely to be the rate determining step in the dissolution of solid UO_3 in SF CO_2 with HTTA and TBP as the extractants. The enhanced dissolution by ultrasound is probably caused by removing the $UO_2(TTA)_2H_2O$ complex from the oxide surface, hence facilitating the process of complex formation. The ensuing TBP adduct formation and dissolution in SF CO_2 is expected to occur rapidly in the system. Demonstration of effective dissolution of uranium oxides in SF CO_2 is important for developing a CO_2-based process for reprocessing spent nuclear fuels.

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REFERENCES

1 Wilson PD (Ed), *The Nuclear Fuel Cycle*, Oxford University Press, Oxford (1996).

2 Weigel F, Katz JJ and Seaborg GT, in *The Chemistry of the Actinide Elements*, Vol 1, 2nd Edn, Ed by Katz JJ, Seaborg GT and Morss LR, Chapman and Hall, London. Chap 7, Plutonium, pp 525 (1986).

3 Smart NG, Wai CM and Phelps CL, Supercritical fluid solutions. *Chem Britain*, pp 34–36 (1998).

4 Laintz KE, Wai CM, Yonker CE and Smith RD, Solubility of fluorinated metal diethyldithiocarbamates in supercritical carbon dioxide. *J Supercrit Fluids* 4:194–198 (1991).

5 Wai CM and Wang S, Supercritical fluid extraction: metals as complexes. *J Chromatography A* **785**:369–383 (1997).

6 Phelps CL, PhD Dissertation, Extraction of uranium from uranium oxides using β-diketones and alkyl phosphates dissolved in supercritical carbon dioxide, University of Idaho, Department of Chemistry (1997).

7 Fritz JS and Jonson-Richard M, Colorimetric uranium determination with Arsenazo. *Anal Chim Acta* **20**:164–171 (1959).

8 Chiarizia R and Horwitz EP, New formulations for iron oxide dissolution. *Hydrometallurgy* **27**:339–360 (1991).

9 Bartle KD, Boddington T, Clifford AA and Hawthorne SB, The effect of solubility on the kinetics of dynamic supercritical fluid extraction. *J Supercrit Fluids* 5:207–214 (1992).

10 Waller B, PhD Dissertation, Equilibrium and dynamic studies of dissolution of uranyl complexes in supercritical carbon dioxide, University of Idaho, Department of Chemistry (1998).

Determination of Partition Coefficients of Crown Ethers between Water and Organic Solvents by Proton Nuclear Magnetic Resonance

*Han-Wen Cheng, Richard Porter, Anne Rustenholtz, and Chien M. Wai**

Department of Chemistry, University of Idaho, Moscow, ID 83844

Abstract

Proton NMR is a simple and rapid method for determining partition coefficients of organic compounds in liquid-liquid extraction. The partition coefficients ($D=[L_{(aq)}]/[L_{(org)}]$) of several crown ethers between water and chloroform/carbon tetrachloride mixtures determined by a proton NMR technique was found to increases exponentially when the carbon tetrachloride percentage in chloroform increases. The crown ether's cavity size does not affect the D value as much as the crown ether's conformation. The partition coefficient depends on solvation environments and may play a significant role in liquid-liquid extraction of metal ions using macrocyclic polyethers as extractants.

Introduction

Crown ethers are the most widely used ligands for selective solvent extraction of metal cations especially for the alkali metals and the alkaline earth metals. Partition of crown ethers between water and organic solvent is one of the key parameters affecting the efficiency of extraction. Several methods have been described in the literature for determination of crown ether partition during liquid-liquid extraction.[1-9] Gravimetric measurement of crown ethers in the organic phase and the aqueous phase of a liquid-liquid extraction system is one of the reported techniques for partition coefficient determination[1-3]. For example, Liu et al. weighed the dry residual in an organic solvent to determine the dissolved crown ether in the organic phase.[1,2] The amount of the crown ether in the aqueous phase was determined by back extraction with CH_2Cl_2 and followed by the same drying and weighing procedures. The partition coefficient was then calculated by taking the ratio of the crown ether concentration in the two phases. Spectrophotometry and conductivity methods were also used for crown ether partition coefficient determination.[4-8] Sadakane et al. concentrated dibenzo-18-crown-6 in the aqueous phase of a benzene/water system by evaporation and then determined the concentration of the crown ether spectrophotometrically at 272nm.[4] Kolthoff and Chantooni back-extracted crown ethers from the aqueous phase of a dichloromethane/water system using sodium and potassium picrates followed by determination of the concentrations of the complexed picrates spectrophotometrically at 370 nm[6-8]. The methods that reported in the literature for crown ether partition coefficient determinations are often time-consuming and subject to large errors. Proton nuclear magnetic resonance (PNMR) is a very sensitive and simple method for determination of crown ethers in water and in organic solvents. Crown ethers usually exhibit simple PNMR spectra, e.g., a single peak for unsubstituted crown ethers such as 12-crown-4 (12C4), 15-crown-5 (15C5), and 18-crown-6 (18C6). The signal-to-noise ratio of a PNMR peak can be improved by multiple scans. Partition of a crown ether between water and organic solvent can be determined by measuring its PNMR peak area in each phase. Such measurements can be done quickly and accurately with a simple sample preparation procedure. This paper describes the results of our recent NMR studies for determining partition coefficients of a number of crown ethers between water and organic solvents such as chloroform and carbon tetrachloride that are commonly used in liquid-liquid extractions. The PNMR technique can also be used to evaluate the solubility of water in the organic phase and its interactions with the dissolved crown ethers.

Experimental Section

Chemicals. The crown ethers 12C4, 15C5, 18C6, and dicyclohexano-18-crown-6 (DCH18C6), as well as acetone-d6 (99.5% D) and carbon tetrachloride were purchased from Aldrich Chemical Company and used without further purification. To carry out the NMR measurement, chloroform was used in the deuterated form (99.8% $CDCl_3$) and was purchased from Isotec INC. The water phase contained 5% D_2O (with 99.8% D in D_2O purchased from SIGMA). All solutions were prepared with deionized water.

For the unsubstituted crown ethers (12C4, 15C5, 18C6), a series of samples were prepared with crown concentrations varying from 0.02 $mol.L^{-1}$ to 0.2 $mol.L^{-1}$ in the deuterated chloroform. The organic solutions were equilibrated with equal volumes of water. For DCH18C6, the concentrations in the organic phase varied from 0.8 $mol.L^{-1}$

to1.2 mol.L^{-1} for the partition coefficient measurements because of its low solubility in water.

Instrumentation. Proton nuclear magnetic resonance measurements were performed using a 500 MHz Bruker DRX500 spectrometer. The pulse interval was set at 11.3 sec (acquisition time 3.3 sec, relaxation delay 8 sec) for obtaining quantitative results. With a scan number of 64, the measurable proton concentration was approximately 1.6×10^{-5} M.

Procedure. Solutions of the crown ethers in the $CDCl_3$ or $CDCl_3$-CCl_4 mixtures were equilibrated with an equal volume (usually 2 mL) of the D_2O-enriched water by shaking with a wrist-type shaker for 2 hours or longer. The mixtures were then centrifuged for 1 hour. The experiments involving crown ethers in chloroform containing high percentages of CCl_4 required longer shaking time (up to 12 hours) to get consistent data. These procedures were conducted at ambient temperatures which were within the range 25±1 °C. Chemical shifts were calibrated by setting the chloroform chemical shift to 7.24 ppm when no carbon tetrachloride was added. Chloroform chemical shifts were corrected by using an insert filled with acetone-d6 in the $CDCl_3$-CCl_4 mixture. The same insert has been used in the 100% CCl_4 organic phase mixture as an external reference and to lock the field. The acetone chemical shift has been set at 2.05 ppm. The intensity of the water peaks in the PNMR spectra were corrected for the 5% D_2O present in the water phase.

Results and Discussion

Typical PNMR spectra for 18C6 in the $CDCl_3$ phase and in the aqueous phase are shown in Figure 1a and 1b. In this experiment, the initial 18C6 concentration in the organic phase was 0.2 mol.L^{-1} in 2 mL of $CDCl_3$. After shaking with 2 mL of water, a part of the 18C6 migrated to the aqueous phase and reached equilibrium with that remaining in the organic phase as shown by the proton resonance peak of 18C6 in the two phases. In this particular experiment, the chemical shift of 18C6 is 3.66 ppm in the $CDCl_3$ phase and 3.58 ppm in the aqueous phase. In addition to the 18C6 resonance peak, a single water peak at 2.67 ppm was also observed in the organic phase. A small $CHCl_3$ peak at 7.24 ppm is also visible which was used to lock the field. For water equilibrated with $CDCl_3$ without 18C6, the water resonance in chloroform occurred at 1.56 ppm. The NMR shift of the water peak in the presence of 18C6 is due to the rapid exchange between free water and complexed water with 18C6 in the organic phase. Water is known to form a 1:1 complex with 18C6 in chloroform and the NMR shift of the water peak is related to the fraction of the crown ether bound with water in the organic phase.[9,10] The amount of free water dissolved in chloroform determined from our NMR experiments is 0.060 ± 0.003 $mol.L^{-1}$ and its chemical shift is 1.6 ppm. In the presence of crown ether such as 18C6 in the organic phase, water dissolved in the organic phase will react with the macrocyclic ligand (L) according to the following equilibrium:

$$H_2O_{org} + L_{org} \rightleftharpoons L{\bullet}H_2O_{org}$$

where subscript org denotes the organic phase. The amount of free water in the organic phase (H_2O_{org}) should remain the same with or without macrocyclic ligand because of the water equilibrium between the aqueous phase and the organic phase. The amount of complexed water ($L{\bullet}H_2O_{org}$) in the organic phase depends on the amount and nature of the crown ether ligand and can be determine by linear regression of the total concentration in water versus the total concentration of ligand at equilibrium. In the case of 18C6, our NMR experiments indicate that about 97% of the macrocyclic ligands are complexed with water in the chloroform phase. The fraction of crown ether bound with water decreases to 54% and 15% for 15C5 and 12C4, respectively, in chloroform. The total amount of water in the organic phase is the sum of the free and the complexed water (H_2O_{org}+ $L{\bullet}H_2O_{org}$) that depends on the amount of a macrocyclic ligand present in the organic phase.

For all of the unsubstituted crown ethers (12C4, 15C5, 18C6), the water phase PNMR spectra contained a measurable single peak for the crown ether and a single peak for the 95% H_2O. The PNMR resonance of water in the aqueous phase is the broad peak at 4.70 ppm shown in Figure 1a. The 18C6 concentration in the aqueous phase can be determined from the ratio of its PNMR resonance to that of the water peak. The concentration of water in the aqueous phase is 52.7 $mol.L^{-1}$ (5% D_2O). The concentration of the macrocyclic ligand in the aqueous phase can be calculated based on this value and the NMR data. The unsubstituted crown ethers are obviously very soluble in water. However, this is not the case for DCH18C6, which is only sparsely soluble in water. In the concentration range 0.02M-0.2M, the DCH18C6 peak in the aqueous phase was not measurable. When the initial concentration of DCH18C6 was increased to the range 0.72M-1.2M in the organic phase, a measurable crown ether peak was observed in the aqueous phase. The solubility of DB24-crown-8 was not high enough to show a measurable PNMR peak in the aqueous phase, even with an initial concentration of 1.0 M in the organic phase.

In the organic phase, we used two different ways to calculate the macrocyclic ligand concentration. The first method involved the addition of a known amount of $CHCl_3$ to $CDCl_3$ to prepare a 0.2 $mol.L^{-1}$ crown ether stock solution. The crown ether concentration was determined from the known $CHCl_3$ concentration and the PNMR intensity ratio of the crown/$CHCl_3$ peaks. The second method was to subtract the crown ether concentration found in the aqueous phase from the initial crown concentration in the organic phase. Both methods gave consistent crown ether concentrations in the organic phase within the experimental errors.

Figure 1 shows the aqueous phase PNMR spectrum of a 0.2 $mol.L^{-1}$ 18C6 in 100% $CDCl_3$ (Figure 1b) and in 50% $CDCl_3$+50% CCl_4 (Figure 1c) after equilibration with water. From the PNMR integration of the crown ether and the water peaks, we calculated the crown ether/water molar ratio in the organic phase. From Figure 1b, the $[18C6]_{org}$ in 100% $CDCl_3$ was found to be 0.047 $mol.L^{-1}$. In a 50:50 $CDCl_3$/CCl_4 solution (Figure 1c), the $[18C6]_{org}$ is increased to 0.104 $mol.L^{-1}$ when the initial concentration remains the same (0.2 $mol.L^{-1}$). It is obvious that a significantly greater amount of 18C6 migrates into the aqueous phase when the solvent contains CCl_4.

The partition of a macrocyclic ligand between water and organic solvent ($L_{org} \leftrightarrow L_{aq}$) is related to the difference in partial molar free energy of the ligand in the two phases. The partition coefficient (D), defined as the equilibrium concentration of crown ether between water and an organic solvent ($D = [L_{(aq)}]/[L_{(org)}]$), can be determined by a plot of $[L_{(aq)}]$ vs. $[L_{(org)}]$ for different crown ether concentrations as shown in Figure 2. In our expression of D, $[L_{(aq)}]$ and $[L_{(org)}]$ represent the crown concentration in the aqueous phase and in the organic phase, respectively, at equilibrium. Figure 2 shows the D values of 18C6 between water and 100% $CDCl_3$, water and 50% $CDCl_3$+ 50% CCl_4 (volume percent) and water and 100% CCl_4. From Figure 2, we can see that the partition coefficient of 18C6 increases by an order of magnitude from 100% $CDCl_3$ to 50%

$CDCl_3$+ 50% CCl_4 and by about two orders of magnitude from 100% $CDCl_3$ to 100% CCl_4.

Based on the experimental D values, the difference in partial molar free energy ΔG for 18C6 between water and chloroform is about 3.54 $kJ.mol^{-1}$ according to the following equation, $\Delta G = -RT \ln D$. In the mixture containing 50% of CCl_4 in $CDCl_3$, the ΔG value becomes -0.39 $kJ.mol^{-1}$. A larger ΔG value corresponds to a greater D value that implies a greater tendency for the crown ether to migrate into the aqueous phase. Figure 3 shows the relationship between the ΔG value and solvent $CDCl_3/CCl_4$ molar ratio.

The partition coefficients of all the crown ethers between water and chloroform determined by the NMR technique are given in Table 1. The partition coefficients of 12C4, 15C5, 18C6 in the concentration region of 0.02 $mol.L^{-1}$ to 0.2 $mol.L^{-1}$ in $CDCl_3$ are 0.25±0.02, 0.175±0.01 and 0.24±0.01, respectively. There is no significant difference between the D values of 12C4 and 18C6, probably because of their even number of oxygen thus allowing the same kind of hydrogen bonding between H_2O and the macrocyclic oxygen atoms in the aqueous phase. 18C6 is known to have a D_{3d} conformation in water according to a molecular dynamics study[11] and an X-ray diffraction study[12] reported in the literature. Water molecules can be hydrogen bonded to the host through every other oxygen atoms forming the crown cavity.[11,12] 15C5 does not have a secondary symmetry axis (C'_2) like 12C4 and 18C6. This would leave less number of water molecules bonded to the cavity with respect to the total number of oxygen in the cavity. However, the lipophilicity of these three crown ethers should be the same considering that their C/O ratio is identical. DCH18-crown-6 is only slightly soluble in water due to its conformation allowing less and weaker hydrogen bonds to water. With

64 scans under our NMR conditions, we could observe a reasonable PNMR peak in the aqueous phase when the initial DCH18C6 concentration was higher than 0.72 mol.L^{-1} in the organic phase. Based on our NMR measurements, the partition coefficient of DCH18C6 between water and chloroform was 0.006±0.002. For DB18C6 and DB24C8, we estimated their D values to be less than 1×10^{-3}.

The distribution coefficient should be independent of solute concentration for dilute solutions. This is true for all the crown ethers studied by this work when the ligand concentration is not more than 0.2 M. When the crown ether concentration becomes very high, the $[L_{(aq)}]$ vs. $[L_{(org)}]$ plot deviates from a straight line. When $[L_{(org)}]$ is close to the solubility limit (i.e. when the initial ligand concentration in the organic phase is more than 0.4 mol.L^{-1}), $[L_{(aq)}]$ increases much faster than $[L_{(org)}]$ when the initial ligand concentration increases. The partition coefficient data for 12C4, 15C5, and 18C6 presented in Table 1 are independent of crown ether concentration up to 0.2 mol.L^{-1} in chloroform. Table 1 shows the partition coefficient of 12C4, 15C4, and 18C6 in mixed $CDCl_3/CCl_4$ solvent systems. For 15-crown-5, the D value changes from 0.175 in pure $CDCl_3$ to 0.290, 0.724, 2.130 and 11.58, when the CCl_4 volume percentage increases to 25%, 50%, 75% and 100%, respectively. Similar trends were also observed for the 12C4 and 18C6 partition coefficients. These results indicate that when the organic solvent polarity decreases, partition of crown ethers into aqueous phase increases. This is reasonable because crown ethers can form hydrogen bonds with water, especially for the unsubstituted crown ethers. Thus when the solvent polarity is reduced, the solubility of the macrocyclic ligands in the organic phase tends to decrease and consequently their distribution in water increases.

The partition coefficient of 18C6 in H_2O/CH_2Cl_2 was reported to be between 0.22[1] and 0.29[7]. This D value is close to our result of 0.24 for 18C6 in $CDCl_3$. The partition coefficient of 18C6 in a non-polar solvent (benzene) was reported to be 17.5[5], which is in the same order of magnitude as that observed in CCl_4 (48.0). This NMR technique can also be used to measure partition coefficients of crown ethers between water and supercritical carbon dioxide. Some preliminary results obtained from a water/supercritical CO_2 system showed that the partition coefficient for 18C6 was measured at 3.72 with 82 atm and 35°C and 0.33 with 259 atm and 35°C. Thus, at low density, the behavior of CO_2 is closer to a non-polar solvent, whereas at high density, its behavior is closer to a polar one. The high-pressure NMR setup and experimental details for the supercritical NMR experiments will be described in a separate paper.

Conclusion

This paper illustrates that PNMR can be used to obtain information regarding crown ether distribution between water and organic solvent and interactions of water with crown ethers in the organic phase. The partition coefficient data of several crowns including 18C6 in chloroform and carbon tetrachloride have been measured using this method. The procedure is simple and partition coefficient data can be obtained rapidly with a good accuracy. The NMR technique for partition studies can also be applied to other ligands of interest to solvent extraction processes, as well as other fluid media such as supercritical CO_2.

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Literature Cited

(1) Inoue, Y.; Amano, F.; Okada, N.; Inada, H.; Ouchi, M.; Tai, A.; Hakushi, T. ; Liu, Y.; Tong, L. H. J. Chem Soc. Perkin Trans. 2, 1990, 1239-1246.

(2) Liu, Y.; Tong, L. H.; Inoue, Y; Hakushi, T. J. Chem Soc. Perkin Trans. 2, 1990, 1247-1253.

(3) Takeda, Y.; Kato, H. Bull. Chem. Soc. Jpn. 1979, 52, 1027-1030.

(4) Sadakane, A.; Iwachido, T.; Tôei, K. Bull. Chem. Soc. Jpn. 1975, 48, 60-63.

(5) Iwachido, T.; Sadakane, A.; Tôei, K. Bull. Chem. Soc. Jpn. 1978, 51, 629-630.

(6) Kolthoff, I. M.; Chantooni, M. K. Jr. J. Chem. Eng. Data 1997, 42, 49-53.

(7) Kolthoff, I. M. Can. J. Chem. 1981, 59, 1548-1551.

(8) Frensdorff, H. K. J. Am. Chem. Soc. 1971, 93, 4684-4688.

(9) De Jong, F.; Reinhoudt, D.N.; Smit, C.J. Tetrahedron Letters, 1976, 17, 1371-1374.

(10) Bryan, S.A.; Willis, R.R.; Moyer, B.A. J. Phys. Chem., 1990, 94, 5230-5233

(11) Ranghino, G.; Romano, S.; Lehn, J.M.; Wipff, G. J. Am. Chem. Soc., 1985, 107, 7873-7877

(12) Mootz, D.; Albert, A.; Schaefgen, S.; Stäben, D. J. Am. Chem. Soc., 1994; 116, 12045-12046.

Figure Captions

Figure 1. Proton NMR of 0.2M 18-crown-6 (initial concentration of the organic phase) in equilibrium with water. (a) Aqueous phase PNMR spectrum; the broad peak at 4.7 ppm is H_2O, (b)PNMR spectrum of the $CDCl_3$ phase; the H_2O resonance peak is at 2.67 ppm, and (c) PNMR spectrum of the organic phase when the solvent composition is 50% $CDCl_3$ + 50% CCl_4 phase instead of 100% $CHCl_3$.

Figure 2. Partition coefficient (D) determination for 18-crown-6 at different $CCl_4/CDCl_3$ ratios:●100% $CDCl_3$, ▲50% $CDCl_3$, ■100% CCl_4

Figure 3. Free Energy (ΔG) versus $CDCl_3$ mole fraction in $CDCl_3/CCl_4$ for 18-crown-6 (●) and 15-crown-5 (O).

Table 1. Partition coefficients and ΔG values for different crown ethers between water and chloroform/carbon tetrachloride at various $CCl_4/CDCl_3$ ratios.

Crown	Solvent % $CDCl_3$[a]	Partition coefficient[d]	Free energy (kJ mol^{-1})[e]
12-crown-4	100% [b]	0.250	3.44
	75% [b]	0.340	2.67
15-crown-5	100% [b]	0.175	4.32
	75% [b]	0.290	3.07
	50% [b]	0.724	0.80
	25% [b]	2.130	-1.87
	0 % [b]	2.450	-6.07
18-crown-6	100% [b]	0.240	3.54
	75% [b]	0.416	2.17
	50% [b]	1.169	-0.39
	25% [b]	3.831	-3.33
	0 % [b]	48.04	-9.60
DCH18-crown-6	100% [c]	0.006	12.68
DB24-crown-8	100% [c]	$<10^{-3}$	>18

[a] Solvent system is $CDCl_3 + CCl_4$ in volume percentage; [b] Initial ligand concentrations are from 0.02 M-0.2 M; [c] Initial ligand concentrations are from 0.72 M-1.2 M.

[d] $D = [L_{(aq)}]/[L_{(org)}]$ and [e] $\Delta G = -RT \ln D$.

Figure 1.

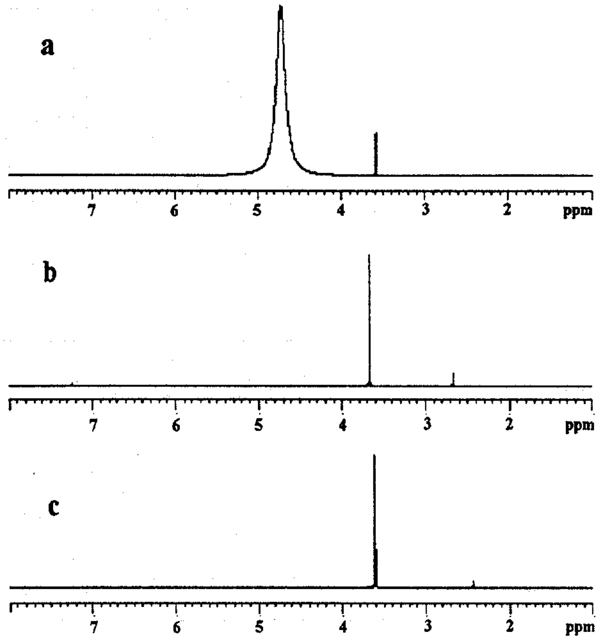
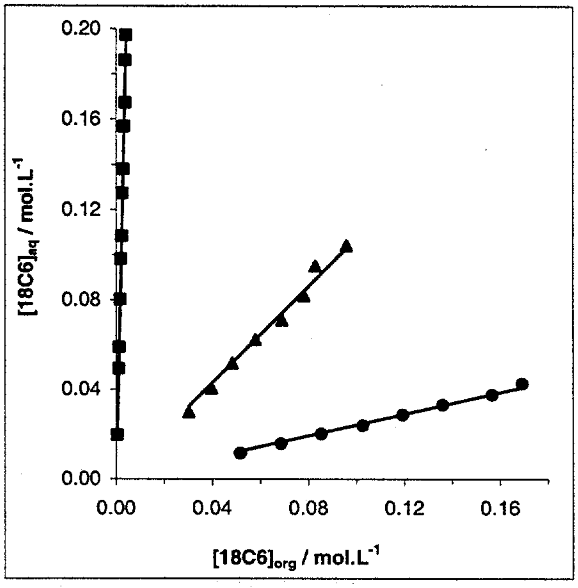
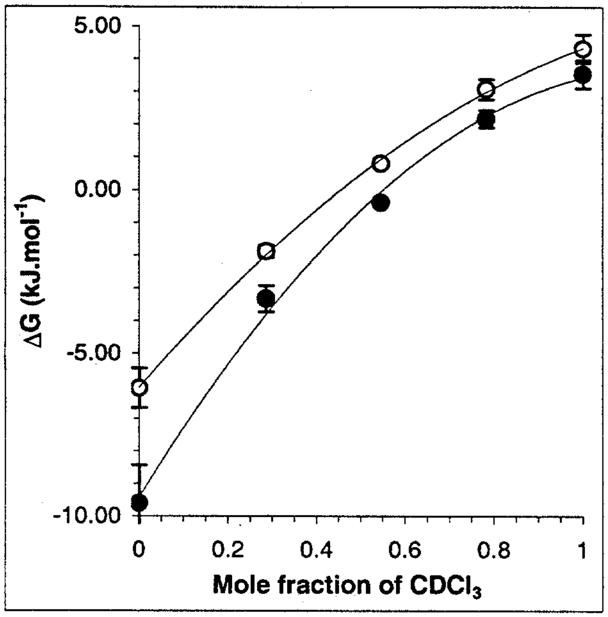


Figure 2.



$[18C6]_{aq}$ / mol.L^{-1}
0.20
0.16
0.12
0.08
0.04
0.00
0.00
0.04
0.08
0.12
0.16
$[18C6]_{org}$ / mol.L^{-1}

Figure 3.


5.00
0.00
-5.00
-10.00
ΔG (kJ.mol^{-1})
0
0.2
0.4
0.6
0.8
1
Mole fraction of CDCl$_3$

Characterization of TBP-HNO_3-H_2O Complex – a New Extractant for Direct Dissolution of UO_2 in Supercritical CO_2

Youichi Enokida[1], Osamu Tomioka[1], Su-Chen Lee[2] and Chien M. Wai[2]
[1]Research Center for Nuclear Materials Recycle, Nagoya University, Nagoya 4648603, Japan
[2]Department of Chemistry, University of Idaho, Moscow, Idaho 83844, USA

Introduction

Recent reports show that tri-n-butyl phosphate (TBP) forms a solution with nitric acid that is soluble in supercritical carbon dioxide (SF-CO_2) and capable of dissolving lanthanide oxides and uranium oxides.[1-5] The ability of this CO_2-philic TBP-HNO_3 solution to dissolve solid uranium dioxide (UO_2) directly in SF CO_2 suggests a potential new technique for reprocessing of spent nuclear fuels and for treatment of nuclear wastes. The UO_2 dissolution process in SF-CO_2 probably involves oxidation of the tetravalent U in UO_2 to the hexavalent $(UO_2)^{2+}$ by nitric acid followed by formation of $UO_2(NO_3)_2 \cdot 2TBP$. The product $UO_2(NO_3)_2 \cdot 2TBP$ identified from the supercritical fluid dissolution process is known to have a very high solubility in CO_2.[6,7]

In the conventional Purex (Plutonium Uranium Extraction) process, aqueous nitric acid (3-6 M) is used to dissolve and oxidize UO_2 in the spent fuel to uranyl ions $(UO_2)^{2+}$. The acid solution is then extracted with TBP in dodecane to remove uranium as $UO_2(NO_3)_2 \cdot 2TBP$ into the organic phase.[8] Direct dissolution of solid UO_2 in SF-CO_2 with a TBP-HNO_3 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 new technology (Super-DIREX process for Supercritical fluid DIRect Extraction process) is currently underway in Japan. This four-year Super-DIREX demonstration project (2002 to 2006) involves a collaboration of three organizations, 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-HNO_3 complex in supercritical CO_2.

The chemical nature of the TBP-HNO_3 complex and the mechanisms of UO_2 dissolution in SF-CO_2 with the TBP-HNO_3 solution are not well known. The TBP-HNO_3 complex is prepared by shaking TBP with a concentrated nitric acid solution. Because water is present in the nitric acid, the complex is expected to have a general formula of $TBP(HNO_3)_x(H_2O)_y$, where x and y can vary depending on the relative amounts of TBP and nitric acid used in the preparation. Within a certain ranges of x, dissolution of the $TBP(HNO_3)_x(H_2O)_y$ complex in supercritical CO_2 was found to cause cloudiness of the supercritical fluid phase indicating formation of small acid water droplets released from the complex due to the anti-solvent effect of supercritical CO_2. In another range of x, cloud formation was not visually observed when the $TBP(HNO_3)_x(H_2O)_y$ complex was dissolved in SF-CO_2. Both types of the $TBP(HNO_3)_x(H_2O)_y$ complex are capable of dissolving solid UO_2 in supercritical CO_2.[3-5]

The solubility of water in pure TBP at room temperature is about 64 grams per liter that is close to a 1:1 mole ratio of TBP/H_2O. In the TBP/H_2O 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_2O in the presence of HNO_3 is unknown. Recent molecular dynamics investigations suggest that hydronium ions or hydrogen from HNO_3 or H_2O are bonded to the oxygen of the P=O bond in TBP[9,10]. Knowledge on the equilibrium compositions of the $TBP(HNO_3)_x(H_2O)_y$ complex prepared by different proportions of the initial TBP and nitric acid is essential for understanding the nature and mechanisms of UO_2 dissolution in SF CO_2.

In this paper, we report our initial results of characterizing the $TBP(HNO_3)_x(H_2O)_y$ complex using several different methods including Karl-Fischer method for determination of H_2O, conventional acid-base titration for measurement of HNO_3, proton nuclear magnetic resonance (PNMR) spectroscopy, and visual observation of phase behavior of the complex in SF-CO_2.

Experimental Section

TBP was purchased from Avocado (Lancs, ordered through Alpha). Nitric acid (69.5 % w/w) was obtained from Fisher Chemical (New Jersey), and was diluted to 15.5 M by deionized water. The $TBP(HNO_3)_x(H_2O)_y$ 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, a portion of the TBP phase was removed using a pipette for characterization experiments.

The concentration of H_2O in the TBP phase was measured by Karl-Fischer titration using an Aquacounter AQ-7 instrument (Hiranuma, Japan). The concentration of HNO_3 in the TBP phase was measured with an automatic titrator (COM-450, Hiranum, Japan) with 0.1 *M* NaOH solution after adding large excess amount of deionized water to the oprganic phase. A 300 MHz NMR spectrometer (BRUKER AMX 300) was used for proton NMR measurements.

Results and Discussion

1. Characterization of the TBP$(HNO_3)_x(H_2O)_y$ complex by titration methods

The amount of HNO_3 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) is expressed in terms of molar concentration of HNO_3 in the TBP phase. The acidity of the equilibrated aqueous phase is also shown in Figure 1 (open circles). A significant fraction of the HNO_3 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 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 This high acidity carried by the TBP phase is useful for dissolving metal oxides in supercritical fluid CO_2.

The experimental data given in Figure 1 can be converted to molar ratios of HNO_3/TBP in both phases. The HNO_3/TBP molar ratio in the organic phase increases rapidly with respect to that in the initial HNO_3/TBP mixture and approaches a value of 2.5 when the initial HNO_3/TBP ratio is 25 as shown in Figure 2. According to Figure 2, more than 2 molecules of HNO_3 can be associated with each TBP molecule in the complex with an initial HNO_3/TBP ratio greater than 8. TBP is a highly CO_2-soluble Lewis base. Inorganic acids such as nitric acid which are usually insoluble in CO_2 can be made soluble by complexation with a CO_2-soluble Lewis base such as TBP. This Lewis base-Lewis acid complex formation approach may provide a method of dispersing various CO_2-insoluble acids in supercritical CO_2 phase for chemical reactions.

An interesting observation is that when the molar ratio of HNO_3/TBP in the organic phase is plotted against the molar ratio of HNO_3/H_2O in the equilibrated aqueous phase, the experimental data appear to show two regions with a breaking point around unity for the HNO_3/TBP ratio (Figure 3). The data seem to suggest that there are two types of the $TBP(HNO_3)_x(H_2O)_y$ complex. Type I would incorporate HNO_3 rapidly into the TBP phase until a 1:1 ratio of HNO_3/TBP is reached. Beyond that point there is another region where incorporating of HNO_3 into TBP becomes slow. Our visual observation indicated that the type I complex would cause cloudiness of the supercritical fluid phase whereas the type II complex would not.

The amount of water in the $TBP(HNO_3)_x(H_2O)_y$ complex determined by Karl-Fischer method also shows two distinct regions. When the molar ratio of HNO_3/H_2O in the TBP phase is plotted against the molar ratio of HNO_3/H_2O in the equilibrated aqueous phase, it clearly shows two different types of the $TBP(HNO_3)_x(H_2O)_y$ (Figure 4). In type I, the ratio of HNO_3/H_2O in the TBP phase tends to increase with increasing HNO_3/H_2O ratio in the aqueous phase. In type II, the ratio of HNO_3/H_2O in the TBP phase maintains a constant value of 3 with increasing HNO_3/H_2O ratio in the aqueous phase. The ratio of HNO_3/TBP in the organic phase increases as shown in Figure 3, but the ratio of HNO_3/H_2O remains constant. It is possible that for the type II complex, the nitric acid incorporated into the TBP phase is probably in a cluster form with a general formula of $(HNO_3)_3H_2O$.

2. Characterization of the complex by proton NMR spectroscopy

Proton NMR spectra of the $TBP(HNO_3)_x(H_2O)_y$ complex at room temperature were taken using an insert technique. Deuterated water (D_2O) was placed in an insert and fitted into an

NMR tube containing a TBP$(HNO_3)_x(H_2O)_y$ complex. The purpose of the D_2O insert was to lock the NMR. A trace amount of HDO present in the deuterated water also allows calibration of the instrument. Other deuterated solvents can also be used for this insert technique. The objective of the NMR study is to investigate the chemical shift of the protons of HNO_3 and H_2O in the TBP$(HNO_3)_x(H_2O)_y$ complex as a probe for the chemical environment of the complex.

A typical PNMR spectrum of TBP$(HNO_3)_x(H_2O)_y$ with a D_2O insert is shown in Figure 5. The singlet peak at 11.95 ppm corresponds to the protons of HNO_3 and water in the TBP phase. H_2O in a TBP-H_2O complex sample shows a singlet resonance peak at 3.85 ppm. In the TBP$(HNO_3)_x(H_2O)_y$ system, this singlet peak shifts up-field with increasing HNO_3 in the system. The NMR shift is attributed to a rapid exchange between the protons of H_2O and that of HNO_3 in the complex. A series of TBP$(HNO_3)_x(H_2O)_y$ samples prepared from different volume ratio of TBP/HNO_3 (15.5M) were studied. All NMR spectra in this series of samples showed a singlet peak for the protons corresponding to HNO_3 and H_2O. The proton NMR shift of the HNO_3/H_2O singlet peak with respect to the molar ratio of HNO_3/TBP in the complex is shown in Figure 6. 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 one. The two regions of the chemical shift observed from the PNMR spectra are consistent with the titration results shown in Figure 4, i.e. there are probably two types of TBP$(HNO_3)_x(H_2O)_y$ complexes depending on the HNO_3/TBP ratio in the complex.

NMR experiments to study the anti-solvent effect of supercritical CO_2 on the TBP$(HNO_3)_x(H_2O)_y$ complex are difficult to carry our at the present time due to the corrosive nature of the solute and the lack of a safe high-pressure NMR device in our laboratory. We chose to use chloroform ($CDCl_3$) to evaluate the anti-solvent effect because chloroform has a small dielectric constant at room temperature (ε=?) close to that of CO_2. Two $TBP(HNO_3)_x(H_2O)_y$ complexes were prepared with the following initial compositions: (i) 2 mL of TBP and 0.456 mL of 15.8 M HNO_3 and (ii) 2.5 mL of TBP and 8 mL of 3.0 M HNO_3. The PNMR spectra of these two $TBP(HNO_3)_x(H_2O)_y$ complexes in $CDCl_3$ are given in Figures 7 and 8. Both PNMR spectra show two peaks in addition to the protons in the butyl group of TBP. The peak at 6.75 ppm in Figure 7 and the peak at 6.18 ppm in Figure 8 are the peaks belonging to the nitric acid droplets formed in the system. The nitric acid droplets are not dissolved in the CDC13 solution. These peaks were identified by a separate NMR study using different concentrations of nitric acid mixed with $CDCl_3$. The nitric acid peak in $CDCl_3$ tends to shift up-field with increasing HNO_3 concentration in the acid solution. The peak at 12.11 ppm in Figure 7 and the peak at 10.03 ppm in Figure 8 are the peaks representing the averaged protons of HNO_3 and H_2O in the complex and the free nitric acid dissolved in the $CDCl_3$ solution. The NMR results obtained from the $CDCl_3/TBP(HNO_3)_x(H_2O)_y$ system, though qualitative in nature, demonstrate the formation of acid droplets from the complex when dissolved in a low dielectric constant solvent due to an anti-solvent effect. The acid droplets probably start with very small particles and aggregated to certain sizes that would make the solution cloudy. These small nitric acid droplets are probably very effective for dissolving solid UO_2 particles.

3. Phase behavior of $TBP(HNO_3)_x(H_2O)_y$ in SF-CO_2

The phase behavior of a $TBP(HNO_3)_x(H_2O)_y$ complex in supercritical CO_2 was also evaluated by visual observation of the solution using a high-pressure view-cell. Figure 7 shows the phase boundaries of the $TBP(HNO_3)_{1.8}(H_2O)_{0.6}$ 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 9 represent the transition pressures from a two-phase region into a single phase solution for the complex with mole fractions greater than 10^{-4}. An interesting observation is that there exists a maximum pressure at a fixed temperature that the complex is homogeneously miscible with SF-CO_2. 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 varying from 11 MPa at 313.15 K to 17 MPa at 333.15 K.

A similar phase behavior was reported for the TBP-CO_2 system.[11] The maximum transition pressure reported for the mixed TBP-CO_2 system at 323.15 K was 11 MPa, lower than the mixed $TBP(HNO_3)_{1.8}(H_2O)_{0.6}$-$CO_2$ 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 9 were obtained by using the same approach described in the literature.[11]

Conclusions

Properties of a Lewis acid-base complex composed of TBP and nitric acid are described in this paper. The complex with a general formula of $TBP(HNO_3)_x(H_2O)_y$ is miscible with SF-CO_2 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 less and one and other greater than one. The former tends to form droplets of nitric acid in SF-CO_2 probably due to the anti-solvent effect of CO_2 and the latter does not exhibit such a behavior. Both types of the $TBP(HNO_3)_x(H_2O)_y$ complex are capable of dissolving solid UO_2 directly in SF-CO_2. This new CO_2-soluble extractant are likely to have important applications in supercritical CO_2 based extraction processes including reprocessing of spent nuclear fuel, treatment of lanthanide and actinide contaminated wastes, and recovery of certain metals from ores and alloys.

Acknowledgment

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References

1. Tomioka, O.; Enokida, Y.; Yamamoto, I. *J. Nucl. Sci. Technol.* **1998**, *35*, 515-516.
2. Tomioka, O. Enokida, Y.; Yamamoto, I. *Sep. Sci. Technol.* **2002**, *37*, 1153-1162.
3. Tomioka, O.; Meguro, Y.; Enokida, Y.; Yoshida, Z.; Yamamoto, I. *J. Nucl. Sci. Technol.* **2001**, *38*, 1097-1102.
4. Samsonov, M.D.; Wai, C.M.; Lee, S.C.; Kulyako, Y.; Smart, N.G. *Chem. Commun.* **2001**, 1868-1869.
5. Enokida, Y.; El-Fatah, S. A.; Wai, C.M. *Ind. Eng. Chem. Res.* **2002**, *41*, 2282-2286.
6. Carrott, M.J.; Waller, B.E.; Smart, N.G., Wai, C.M. *Chem. Commun.* **1998**, 373-374.
7. Carrott, M.J.; Wai, C.M. *Anal. Chem.* **1998**, *70*, 2421-2425.
8. Wilson, P.D. (Ed) *Nuclear Fuel Cycle, From Ore to Waste*, **1996**, Oxford Science Publications.
9. Baaden, M.; Schurhammer, R.; Wip~~p~~ff, G. *J. Phys. Chem. B* **2002**, *106*, 434-441.
10. Schurhammer, R.; Wipff, G. *New J. Chem.* **2002**, *26*, 229-233.
11. Joung, S.N.; Kim, S.J.; Yoo, K.P. *J. Chem. Eng. Data* **1999**, *44*, 1034-1036.

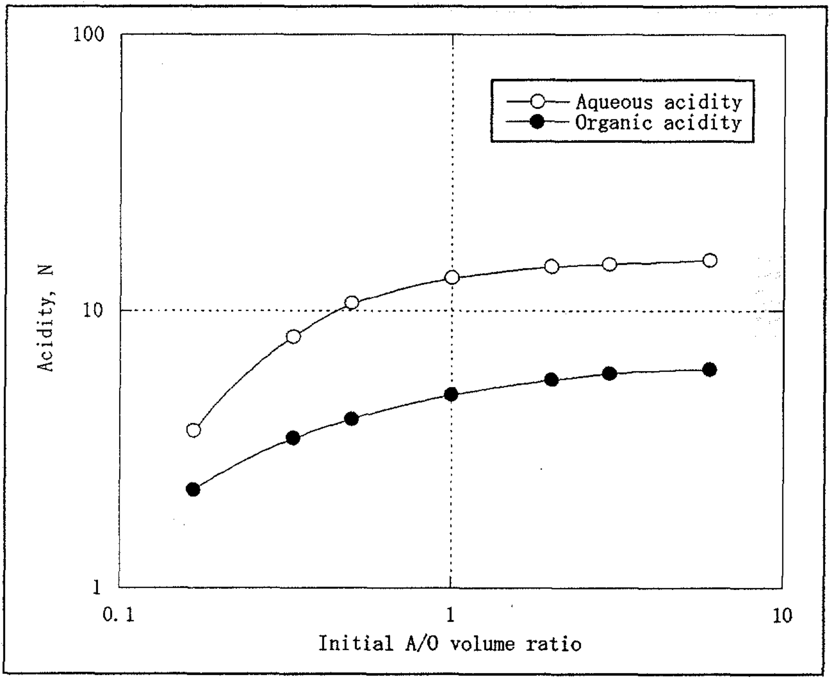

Figure 1. Acidities of the aqueous and the organic phase
The x-axis is the initial volume ratios of 15.5 M HNO_3 to 98% TBP.
◊, Aqueous acidity, is defined as (moles of H^+) / (L of aqueous solution).
♦, Organic acidity, is defined as (moles of H^+) / (L of organic solution).

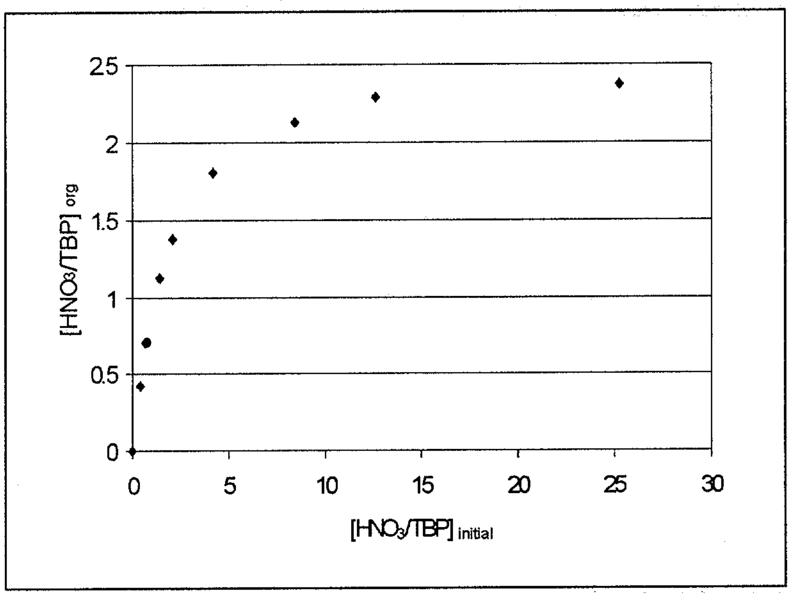

Figure 2 Ratio of $[HNO_3]/[TBP]$ in the TBP phase as a function of the initial $[HNO_3/TBP]$ ratio in sample preparation

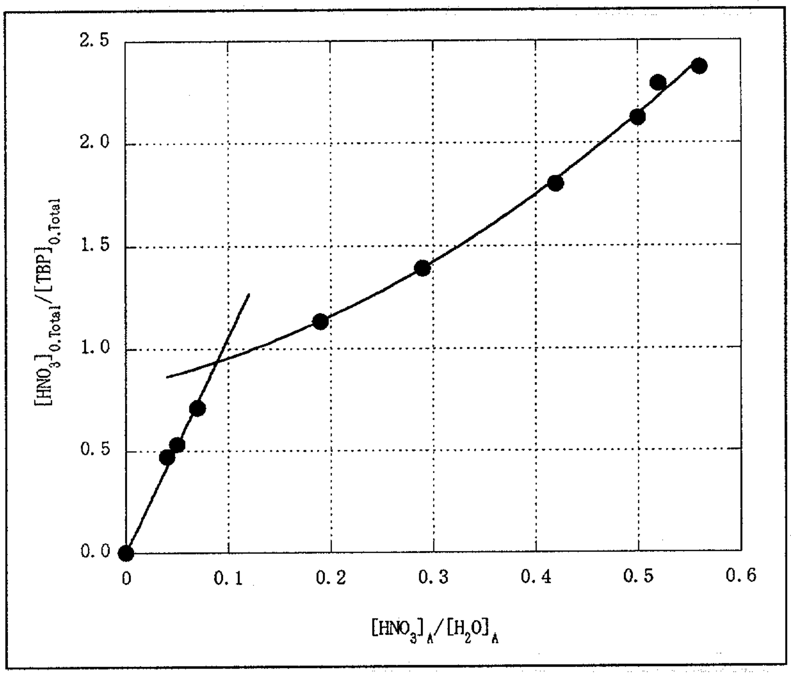

Figure 3. A plot of $[HNO_3]/[TBP]$ ratio in the TBP phase against $[HNO_3]/[H_2O]$ ratio in the equilibrated aqueous phase.

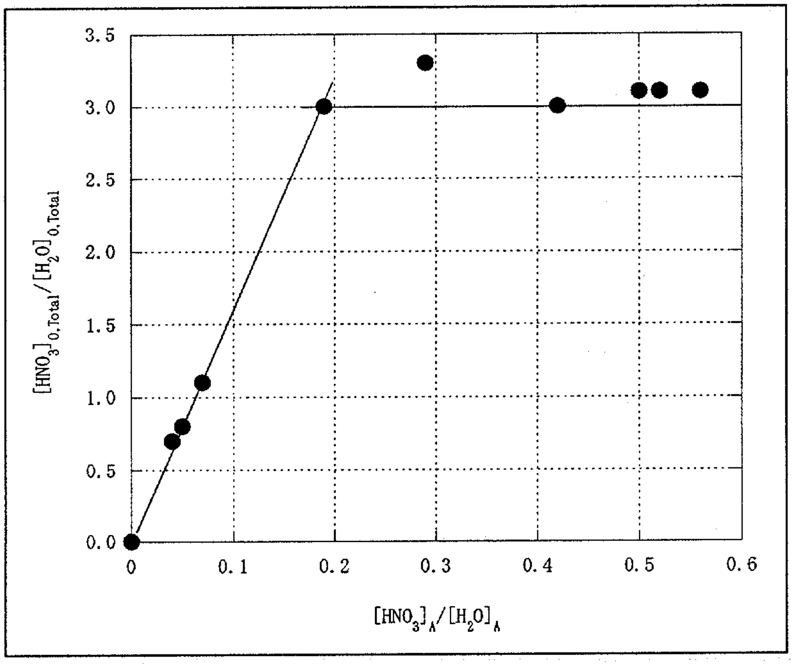

Figure 4. Molecular ratio of $[HNO_3]/[H_2O]$ in the TBP phase versus that in the equilibrated aqueous phase

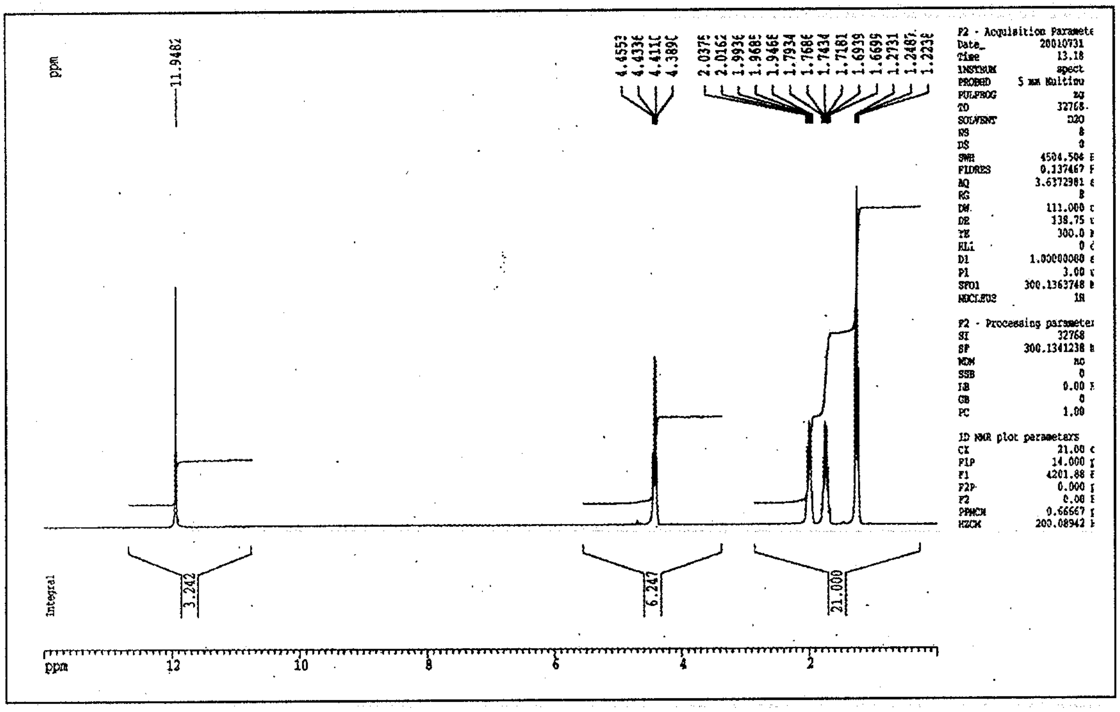

Figure 5. A typical 300 MHz proton NMR spectrum of $TBP(HNO_3)_1(H_2O)_y$ with a D_2O insert. This sample was prepared by mixing 2.0 mL of 15.5M HNO_3 with 1.0 mL of 98% TBP.

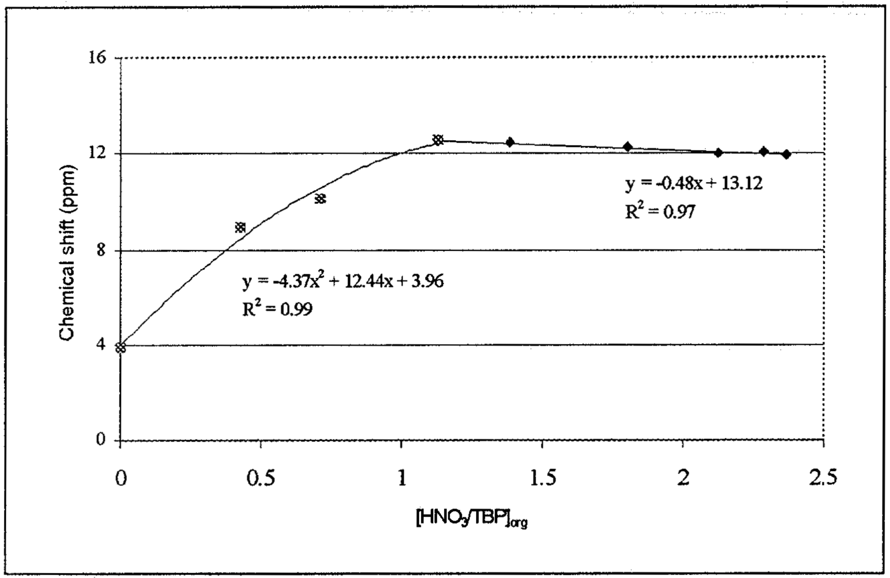

Figure 6. Chemical shift (ppm) with respect to molar ratio of HNO_3/TBP in $TBP(HNO_3)x(H_2O)_y$

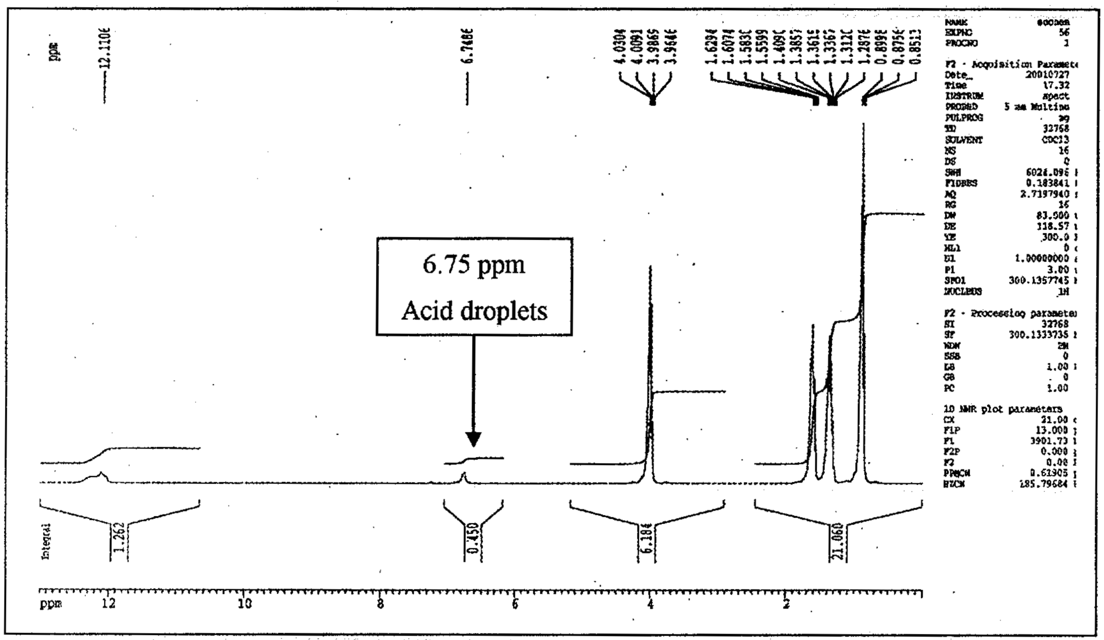

Figure 7. ^{1}H 300 MHz NMR spectrum of TBP·xHNO$_3$·yH$_2$O in CDCl$_3$

The TBP·xHNO$_3$·yH$_2$O is prepared by mixing 2.0 mL of 98 % TBP and 0.456 mL of 15.8 M HNO$_3$. The volume ratio of TBP·xHNO$_3$·yH$_2$O to CDCl$_3$ is 1:5.

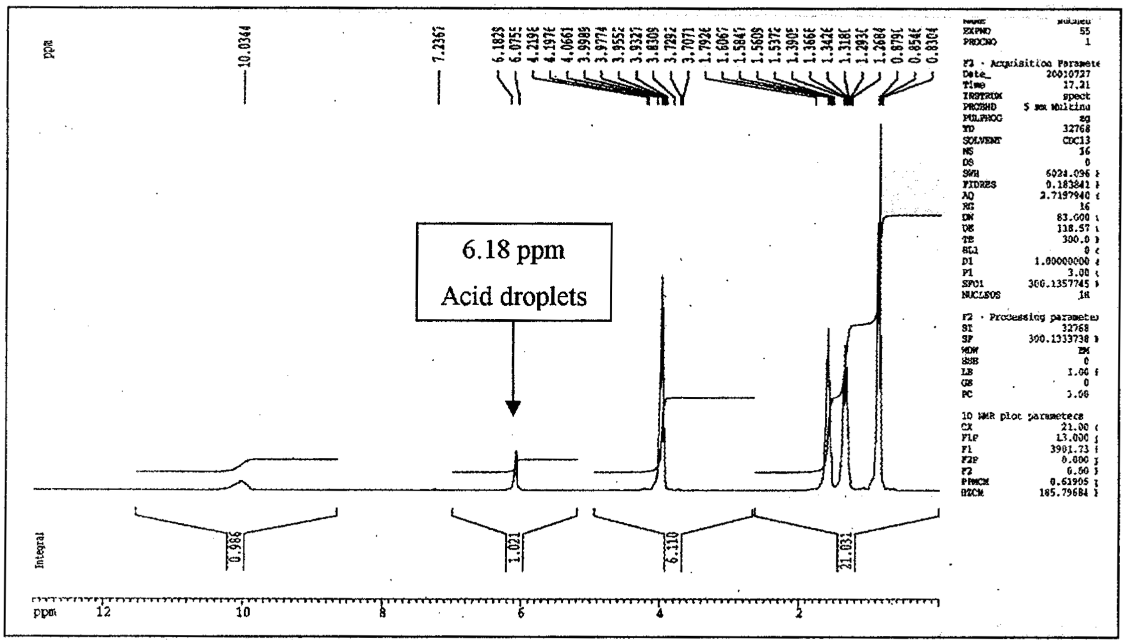

Figure 8. ^{1}H 300 MHz NMR spectrum of TBP·xHNO$_3$·yH$_2$O in CDCl$_3$

The TBP·xHNO$_3$·yH$_2$O is prepared by mixing 2.5 mL of 98 % TBP and 8.0 mL of 3.0 M HNO$_3$. The volume ratio of TBP·xHNO$_3$·yH$_2$O to CDCl$_3$ is 1:5.

An FT-IR study of Crown Ether Complexation with Water in Liquid and Supercritical CO_2

Anne Rustenholtz[I], *John L. Fulton*[II] *and Chien M. Wai*[I*]

[I]Department of Chemistry, University of Idaho, Moscow, ID 83844-2343

[II]Fundamental Science Division, Pacific Northwest National Laboratory, P.O. Box 999 MS P8-19, Richland, WA 99352

Introduction

Supercritical fluids recently tend to be preferred to conventional solvents for the extraction of metals or ions. Because of their high volatility, the extracted species, easily freed of solvent contamination, can be retrieving without any difficulties and no arm for the environment. The most common of those fluids, carbon dioxide, has numerous advantages: Its low toxicity and its easiness to reuse make it an environmentally acceptable solvent; Its cost is low and its availability in pure form is large; It has convenient critical properties (T_c=31 °C and P_c=73.7 bar) and its solvation strength varies with density. This last advantage allows the study of solvation effects by a simple tune of the pressure and/or the temperature.

Supercritical Fluids Extraction (SFE) of metals and ions, due to the weak solute to CO_2 interaction, requires a chelating agent to increase the solubility[1-3]. Macrocyclic ligands, like crown ethers have been intensively used for the extraction of alkali cations, such as Li^+, Na^+ and Cs^+ into organic solvents.[refs2] Their efficiency is undeniable and their relatively high solubility in liquid and supercritical CO_2 make them a perfect chelating agent for cesium extraction.

Metallic ions are most of the time extracted from aqueous solutions. This implies that the organic or fluid phase can be charged with water. The water content, in the fluid phase, has a direct influence on the extraction process.[2, 11] It has been reported that the extraction efficiency of alkali metal ions increases with the solubility of water in the organic phase using macrocyclic polyethers as a chelating agent.[11] In CO_2, the water solubility can be compared to the extracted and extractant species in solution. Therefore, its influence has to be considered. With crown ethers, both computational simulation[12] and spectroscopic[13,14] reports show that in organic solvents, the water can be bonded to the crown ether by two different kinds of hydrogen bonding. The first one, outside the cavity, is composed by a single hydrogen bond between one hydrogen atom that belongs to the water and one crown ether oxygen atom. The second one, inside the cavity, is composed by a water bridge between the two water hydrogen atoms and two different crown ether oxygen atoms.

FT-IR is a sensitive and qualitative technique that has been used during the past years to study hydrogen bonding in different solvents[14-17]. Keith P. Johnston and al. used it to understand the solvent effect on hydrogen bonding in supercritical fluids[15]. They have been able to determine, with a good accuracy, the equilibrium constants and other thermodynamics data for the hydrogen bond between methanol and triethylamine. This technique has also been used by Moyer and al.[14] to see how water is bonded to crown ethers in carbon tetrachloride. They attributed the free and bonded water bands to the two different kinds of hydrogen bonds mentioned above.

No one has studied these interactions, which are a good basis to further experiments including alkali ions salts, in a supercritical fluid such as CO_2.

Experimental Section

A specially design high-pressure cell that can hold a pressure of 500 bars has been used for this study. The 9.2mL internal volume cell is built in stainless steel block. The infrared beam is focused along two conical holes and passes through two diamond windows 100µm apart. The cell has one observation sapphire window sealed with a gold-plated metal V-ring seal, that allows the determination of the number of phase present inside the cell. For quantitative analysis and to be certain that there is any aqueous phase on the beam path windows, which would alter the data, it is important to be assured that only one phase is inside the cell. A Teflon coated magnetic stirring bar was introduced into the cell allowing the stirring of the solution while the cell was placed inside the spectrometer.

An ISCO syringe pump has been used to control and directly supply with liquid CO_2 the cell preloaded with the studied chemicals. The pressure was measured by an electronic transducer from Precise sensor Inc 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 monitored by Watlow Winoma controller with a ± 1 °C accuracy. A Bruker IFS 66v FT-IR spectrometer couple to a Kolmar Technologies mercury-cadmium-telluride (MCT) dual channel detector has been used to acquire all IR spectra. In order to obtain a good signal to noise ratio, the acquisition time was set to 5 min (corresponding to approximately 2350 scans), the scanner velocity was 80kHz and the wavenumber resolution was 4 cm^{-1}. The background of the empty cell composed by the diamond windows signal as been subtracted from each spectrum and renewed each time that the cell moved.

Deutered water has been used rather than H_2O to avoid overlapping of water and CO_2 absorbance bands between 3500 and 3800 cm^{-1}. Those bands have a too high absorbance to be subtracted without a lost in the D_2O signal.

D_2O (100% d, 99.96% pure) and 18-Crown-6 (99.5% pure) has been purchased from Aldrich Chemicals Company and used without further purification. Carbon dioxide was supplied in Supercritical fluid chromatography (SFC) grade (purity >99.99%) from Scott Specialty gases Inc.

Pure CO_2 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 bars. Pure CO_2 density has been determined using reported table[18].

To avoid water contamination from the atmosphere, the cell has been purged with nitrogen and the chemicals have been introduced under a glove box containing nitrogen. The solutions have been stirred during 20 to 30 minutes in order to reach the equilibrium after each density or concentrations changes. Longer equilibrium times have been tried out with no significant change in the IR spectra and intensities. For one crown ether and one D_2O concentrations, different spectra have been taken by increasing the amount of CO_2 inside the cell using the syringe pump and without reloaded the cell with new reactants. The cell has been cleaned between each experiment with liquid and supercritical CO_2 until no trace of D_2O or crown ether have been found. When the crown ether, which can stick to the cell walls and windows, couldn't be removed in this way, methanol and water have been used to clean the cell. It has been dried and purged several times with CO_2 before further use. Experiments have been scheduled with an increase of the crown ether concentration as an other precaution to minimize an eventual crown ether contamination.

Curve fitting and other spectrum analysis and corrections have been performed with the latest version of OPUS (Bruker Optiks) software

Results and Discussion

For this study, the crown ether concentration in CO_2 varies from 0 to 0.6 $mol.L^{-1}$ whereas the total D_2O concentration varies from 16 to 100 $mmol.L^{-1}$. With these concentration ranges, the total D_2O amount dissolved in CO_2 stays under the solubility limits reported in the literature for water[19,20]. This fact has been confirmed by a one-phase observation inside the cell with pure DO2 dissolved in different CO_2 densities.

Because of two small 18-crown-6 bands at 2810 and 2770 cm^{-1}, which are overlapping the D_2O signal, the spectrum of pure crown ether in CO_2, at the same temperature and pressure than the D_2O and 18-crown-6 mixtures, has been subtracted before analysis.

On figure 1, spectra for different crown ether concentrations (0 to 0.6 mol.L^{-1}) and one fixed D_2O concentration (0.049 mol.L^{-1}) are showed in liquid (a) and supercritical (b) CO_2. The peak for free D_2O (OD asymmetric at 2761 cm^{-1} and symmetric at 2654 cm^{-1} stretches) can be easily determined from the heavy water spectra and are in accordance with the litterature[22] (i.e. 2789 and 2666 cm^{-1} for the D_2O vapor). When 18-crown-6 is added to the solutions, three other peaks at 2733, 2679 and 2590 cm^{-1} appear. According to the peak assignment of water complexed to crown ether in carbon tetrachloride performed by Moyer et al.[14], the broad peak at 2590 cm^{-1} correspond to the symmetrical stretch of the OD bond involved in the hydrogen bridge showed on figure 0a. The sharp OD band at 2733 cm^{-1} belongs to the unbounded OD stretch on figure 0b. An isobestic point is found at 2744cm^{-1} between this band and the free OD asymmetrical stretch. This point connotes the formation of an 1:1 crown ether complex with water. When the 18-crown-6 concentration overpass 0.5 mol.L^{-1}, the isobestic point is no longer align with the spectrum. This phenomenon can be seen on figure 1 for the 0.6 mol.L^{-1} crown ether concentration. This can be explain by the apparition of a 1:2 complex between 18-crown-6 and heavy water and it is confirmed with the non-consistent equilibrium constant calculation at this concentration. The bonded OD stretching band on figure 0b is found at 2679 cm^{-1} between the symmetrical and the asymmetrical free water stretches bands unlike Moyer results where it had been found at lower energy than the symmetrical free water peak. In order to exonerate our experiment setup and chemicals from this difference, some experiments has been run in carbon tetrachloride between 18-crown-6 and both H_2O and D_2O. The band in question, was found at the lower energy, for all experiments in CCl_4, as reported by Moyer. This difference is entirely due to the solvent and shows once again the particularity of supercritical fluids.

Molar absorptivities have been calculated for each fluid condition, because of their change with CO_2 density[21]. The molar absorptivities for free D_2O (table 1 and/or figure 2) has been determined by the analyse of FT-IR spectra with pure D_2O at known concentrations whereas the total bonded water concentration, for equilibrium constant calculations has been deducted from them. The molar absoptivity of D_2O, as reported for pyrene and anthracene[21], in liquid and supercritical CO_2 increases with the fluid density. Its value is more than doubled for both free D_2O peaks in the 0.66 to 1.04 $g.mL^{-1}$ density domain.

The formation of a 1:1 complex between 18-crown-6 and water in the CO_2 phase, as reported for some organic solvents[refs], is confirmed by the analysis of the data and the determination of the equilibrium constant K relative to the following equation:

$$18C6 + D_2O \leftrightarrows 18C6.D_2O \qquad (1)$$

$$K=[18C6.D_2O]/([18C6][D_2O]) \qquad (2)$$

The K value varies considerably with CO_2 density (figure 3). At constant pressure (200bar), this value decreases from 19.7 to 12.0 $L.mol^{-1}$ with an increase of the temperature (from 25 to 60°C). The same trend is noticed with an increase of the pressure at constant temperature (i.e. from16.8 to 12.0 $L.mol^{-1}$ at 40°C and between 200 and 400 bar). These values are comparable to the one found by Moyer et al. (i.e. 15.6 (1.2) $L.mol^{-1}$) in carbon tetrachloride. This implies that, when it concerns hydrogen bonding, liquid and supercritical CO_2 behave as a non-polar solvent such as CCl_4 and not like chloroform as usually considered.

The molar enthalpy of the hydrogen bonding (ΔH) can be determined from the equilibrium constant at constant pressure by using the equation (4) established by Johnston and all[ref] from well known thermodynamic relations (equations 3). T is the temperature in K and R the gas constant.

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -\Delta S = \frac{\Delta G - \Delta H}{T} \quad \textit{and} \quad \Delta G° = -RT \ln K \qquad (3)$$

$$\left(\frac{\partial(\ln K)}{\partial 1/T}\right)_P = -\frac{\Delta H}{T} \qquad (4)$$

Using a linear regression on the plot of lnK versus 1/T (figure 4), and presuming that ΔH is temperature-independent, ΔH has been found to be –10.3 $kJ.mol^{-1}$ at 200 bar. The process is exothermic as expected for a hydrogen bonding process at relatively high pressure in supercritical fluids.

To conclude this report, it would be interesting to see how the absorbance of two water to crown isomers described before behave in regard to pressure and temperature changes. When the temperature is increased from 25 to 60°C, at the same pressure (i.e. 200 bar), both isomers concentration increases. Nevertheless, a larger increase is noticed for the peak with a single hydrogen bond between crown ether and D_2O. The same trend is observed when the density increases (by increase of the pressure from 200 to 400 bar) at constant temperature (i.e. 40°C).

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Legend

Figure 1. FT-IR spectra of free and bonded D_2O at different 18-crown-6 concentrations (0 to 0.6 mol.L^{-1}) and at one fixed D_2O concentration (0.049 mol.L^{-1}) in liquid (a: 25°C and 200 bar) and Supercritical (b: 35°C and 200 bar) CO_2.

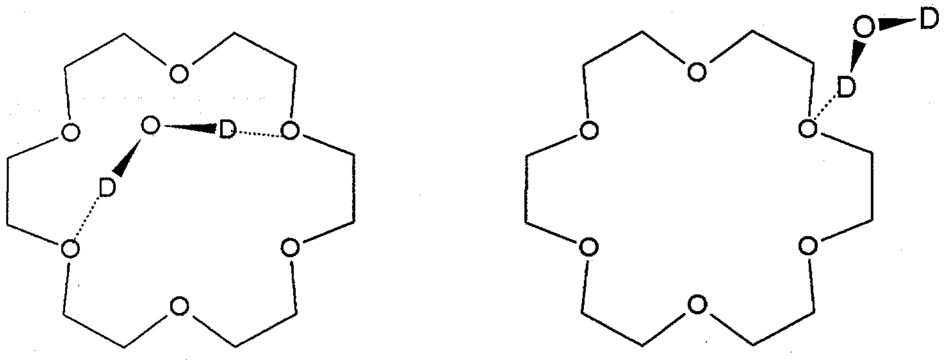
Table 1: Molar Absoptivity for free D_2O asymmetric (ε_1 at 2761 cm^{-1}) and symmetric (ε_2 at 2654 cm^{-1}) stretching bands at different CO_2 density.

Figure 2: Molar Absoptivity for free D_2O asymmetric (ε_1 at 2761 cm^{-1} (●)) and symmetric (ε_2 at 2654 cm^{-1} (○)) stretching bands at different CO_2 density.

Figure 3: Density effect on the equilibrium constant (K).

Figure 4: Dependence of lnK on 1000/T at 200 bar.

Figure 0



a) b)

Figure 1

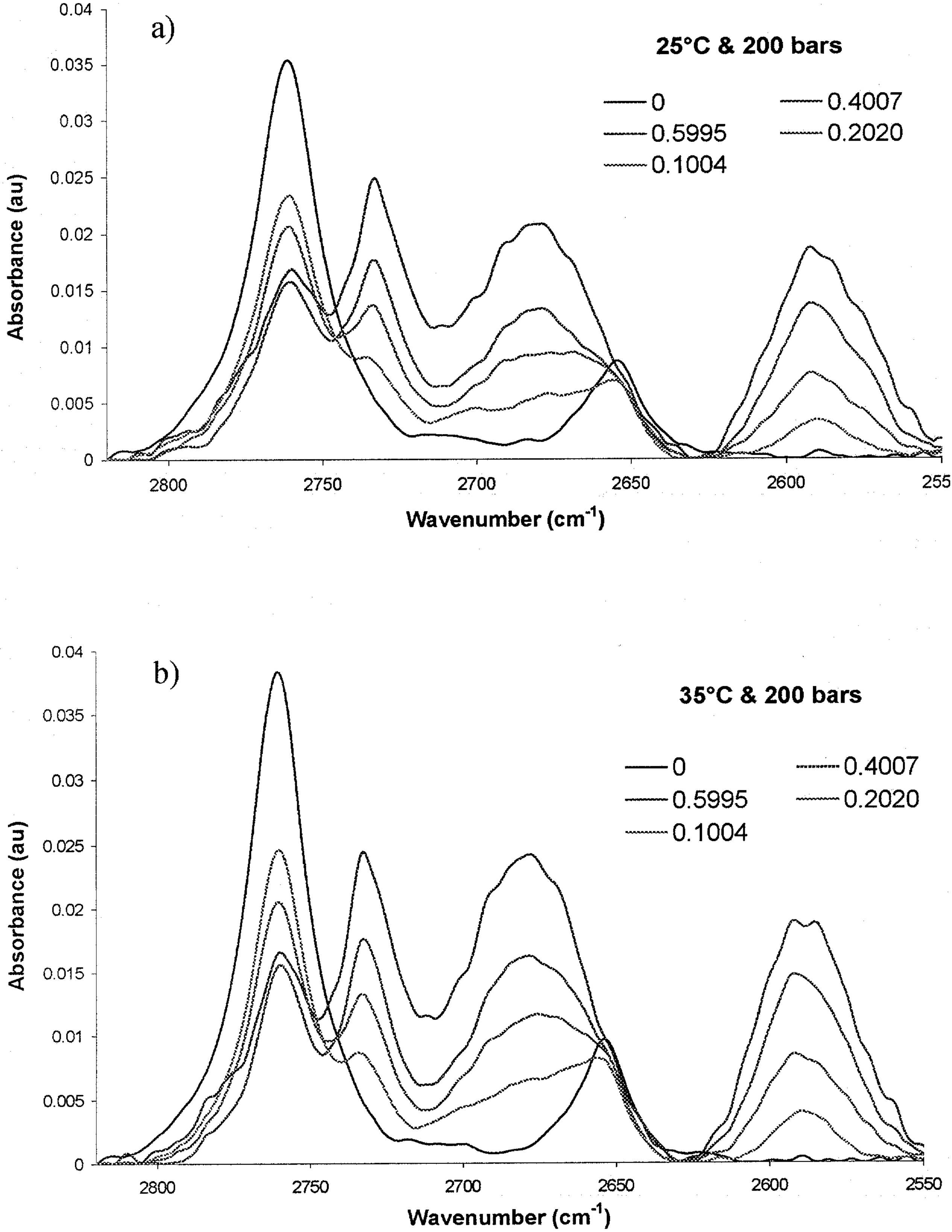

a)
25°C & 200 bars
0
0.4007
0.5995
0.2020
0.1004
Absorbance (au)
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
2800
2750
2700
2650
2600
2550
Wavenumber (cm^{-1})
b)
35°C & 200 bars
0
0.4007
0.5995
0.2020
0.1004
Absorbance (au)
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
2800
2750
2700
2650
2600
2550
Wavenumber (cm^{-1})

Table 1

Pressure (bar)	199	199	200	199	200	200	199	199	301	352	403	403
Temperature (°C)	70	60	50	40	35	33	31	25	40	40	40	25
Density (g.mL^{-1})	0.659	0.723	0.784	0.840	0.860	0.870	0.888	0.914	0.911	0.930	0.957	1.035
ε_1 (L.mol^{-1}.cm^{-1})	44.90	52.32	60.41	68.47	72.78	74.34	80.18	79.22	73.93	77.89	81.04	92.88
ε_2 (L.mol^{-1}.cm^{-1})	9.81	11.40	13.41	15.96	17.17	17.54	19.69	19.51	17.84	19.12	20.00	23.65

Figure 2

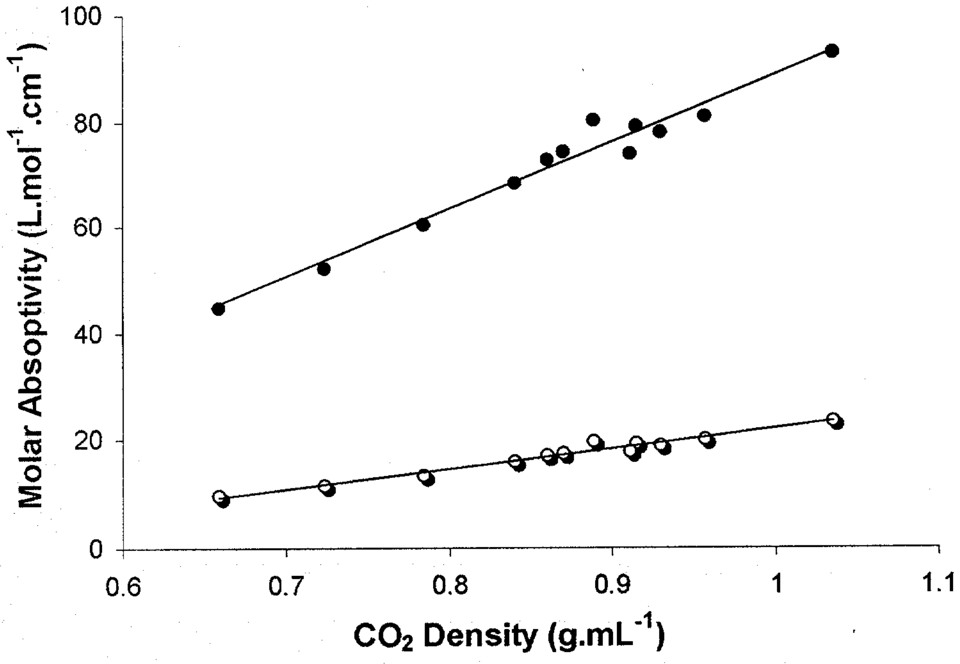


Figure 3

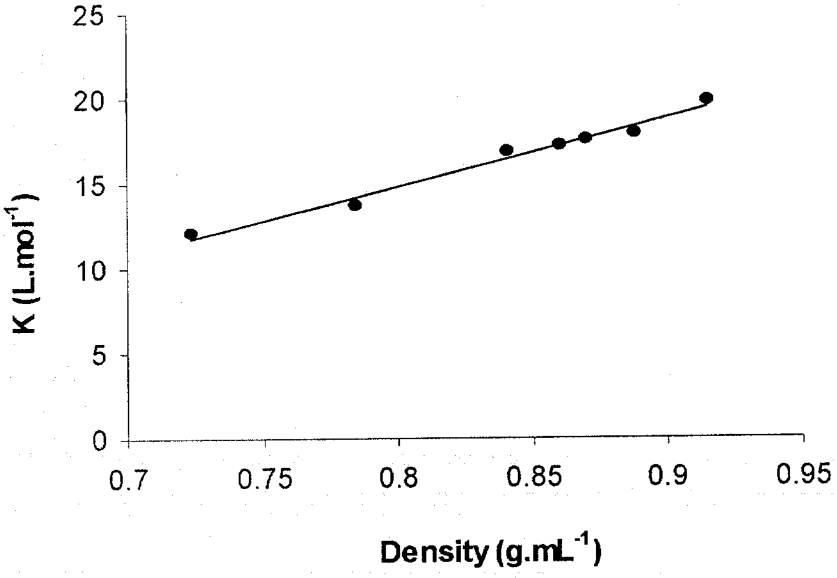


Figure 4