High solubility of $UO_2(NO_3)_2 \cdot 2TBP$ complex in supercritical CO_2

Mike J. Carrott,[a] **Brenda E. Waller,**[a] **Neil G. Smart**[b] **and Chien M. Wai***[a]

[a] *Department of Chemistry, University of Idaho, Moscow, ID 83844, USA*
[b] *Research and Technology, BNFL, Sellafield, Cumbria, UK CA20 1PG*

$UO_2(NO_3)_2 \cdot 2TBP$ is highly soluble in supercritical CO_2, with concentrations of 0.0025–0.4981 M attainable at modest temperatures and pressures, demonstrating that supercritical CO_2 can provide a viable substitute for organic solvents used in nuclear fuel processing.

Recently there has been growing interest in the use of supercritical CO_2 for extracting metals and radioisotopes from waste materials. This technology is particularly attractive to the nuclear industry, where the replacement of organic solvents with supercritical CO_2 has the potential to minimize or eliminate the secondary waste produced by conventional extraction techniques, such as the PUREX process. Metal ions in solid and liquid matrices can be extracted by supercritical CO_2 using the *in situ* chelation method originally reported by Wai and coworkers.[1] This method neutralizes the charge on the metal using organic ligands dissolved in supercritical CO_2, to produce soluble metal chelates. A recent review reported the solubility data available to date for 49 metal chelates in CO_2,[2] however, the low solubility of many metal chelates in supercritical CO_2 is a major limitation of this method for practical metal processing. This problem has been partially overcome by the use of fluorinated ligands which have been shown to enhance the solubility of the resulting metal chelate by over two orders of magnitude.[3] Supercritical CO_2 has already been successfully applied to the extraction of U, Th and lanthanides from liquid and solid matrices using fluorinated β-diketone ligands.[4,5] Recent work has shown that UO_2^{2+} and Th^{4+} can be effectively extracted from nitric acid solution using CO_2 modified with tributylphosphate (TBP).[6,7] The uranyl species extracted by supercritical CO_2 is a neutral uranyl nitrate–TBP complex, $UO_2(NO_3)_2 \cdot 2TBP$, which is identical to the species extracted in the PUREX process using 20% TBP in kerosene.

SFE offers several advantages over conventional solvents employed in the PUREX process, the most important of which is the potential to minimize the amount of secondary waste generated by reprocessing spent fuel. Since the solvating power of supercritical CO_2 is density dependent, extracted species are easily recovered by expanding the fluid to atmospheric pressure, thus precipitating the solutes and allowing the CO_2 to be recycled. In addition CO_2 is inexpensive, non-toxic and stable under high radiation.

In order to develop models for the extraction process and assess the feasibility of using CO_2 to replace organic solvents in the PUREX process, solubility data for the complex in supercritical CO_2 is essential. Here we report the first solubility measurements for $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2.

$UO_2(NO_3)_2 \cdot 2TBP$ was prepared using a similar method reported for the synthesis of the triphenylphosphine analog.[8] Approximately 2 g of $UO_2(NO_3)_2 \cdot 6H_2O$ were placed in a 200 ml round bottomed flask, 2 mol equiv. of TBP in 100 ml hexane were added and the mixture stirred for *ca.* 2 h at room temperature. When the uranyl nitrate had dissolved, the organic phase was separated from the water of hydration displaced by TBP, and the solvent evaporated to yield the product as a viscous yellow oil. The product was further purified by dissolving in *ca.* 15 ml hexane, freezing to −50 °C to crystallize

the complex and cold filtering. This process was repeated three times to remove excess TBP. Thin film IR spectra of the liquid phase were obtained using NaCl plates; cm^{-1}: 2962s, 2878s, 1526s, 1355w, 1281m, 1192s, 939m, and the absorption bands are in good agreement with those reported by Auwer *et al.*[9]

The solubility of $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 was determined by UV–VIS spectroscopy,† over a pressure range of 100–300 atm and at temperatures of 40, 50 and 60 °C. Prior to the solubility measurements the molar absorptivity of the complex at 411 nm was determined using standards of $UO_2(NO_3)_2 \cdot 2TBP$ in hexane,‡ and found to be 8.77 l mol^{-1} cm^{-1} at 411 nm. Using Beer–Lambert's law the concentration of the complex in supercritical CO_2 was calculated from subsequent spectroscopic measurements. A typical UV–VIS spectrum of $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 is shown in Fig. 1. The solubility curves for $UO_2(NO_3)_2 \cdot 2TBP$ under the conditions investigated are presented in Fig. 2. It can clearly be seen that the solubility of the complex increases dramatically with pressure, particularly at low temperatures. At 40 °C the concentration of $UO_2(NO_3)_2 \cdot 2TBP$ in CO_2 increases from 0.0025 M at 100 atm to 0.4291 M at 225 atm, corresponding to 2.31 and 397.3 g l^{-1} respectively, and represents an increase in
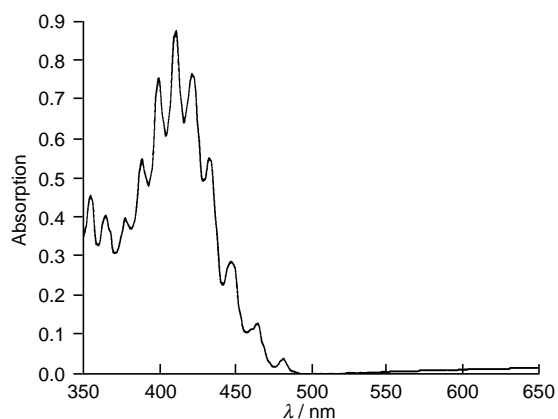

Fig. 1 UV–VIS spectrum of $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2

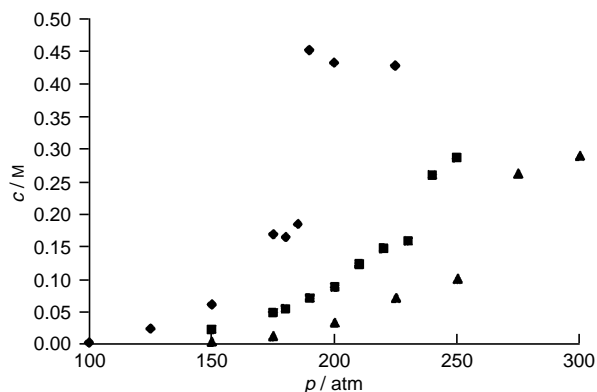**Fig. 2** Solubility of $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 at 40 °C (◆), 50 °C (■) and 60 °C (▲)

solubility over two orders of magnitude. Similar curves were obtained at 50 and 60 °C, although the solubility was observed to decrease with increasing temperature. This effect is due to the lower density and hence decreased solvating power of the fluid at higher temperatures. At 50 and 60 °C no appreciable solubility (< 0.001 M) was observed below 125 atm, but the concentration of $UO_2(NO_3)_2 \cdot 2TBP$ increased rapidly in excess of 0.2 M at 240 and 275 atm, respectively. The use of a high pressure view cell as a saturation vessel enabled the phase behaviour of the complex to be observed during the spectroscopic measurements. Initially two distinct phases were present, an intense yellow liquid (lower) phase due to the complex and a pale yellow supercritical (upper) phase due to the CO_2 saturated with $UO_2(NO_3)_2 \cdot 2TBP$. With increasing pressure the yellow colour of the supercritical phase became progressively more intense due to the increasing solubility of the complex, also the liquid phase became darker in colour until it appeared almost black, possibly due to CO_2 being dissolved in the liquid phase. Further increases in pressure produced a very turbid, opaque (almost black) phase in which the meniscus had virtually disappeared, and eventually resulted in an intense yellow single phase. This transition to a single phase occurred very rapidly, over a small pressure range, and is apparent from the sharp increases in concentration observed at 190, 240 and 275 atm for the solubility curves at 40, 50 and 60 °C, respectively. Upon formation of a single phase the concentration remained constant with further increases in pressure, and the solubility curve reached a plateau due to complete dissolution of the complex. Valid solubility data cannot be obtained after this point as the CO_2 was no longer saturated with the complex. Since uranyl nitrate itself is insoluble in pure CO_2 the high solubility of the complex can be attributed to the shielding of the central metal ion by the TBP ligands and increased solute–solvent interactions between the butyl groups and CO_2.

In conclusion, this study has shown that it is possible to obtain extremely high concentrations of $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2, which surpasses the solubility of any metal chelate previously reported in the literature.§ Most significantly, the concentrations of $UO_2(NO_3)_2 \cdot 2TBP$ in supercritical CO_2 are comparable to those encountered in the waste streams of the PUREX process, typically 0.13–0.47 M in the organic phase.[10] In conjunction with previous extraction work,[6,7] this clearly demonstrates CO_2 can offer a viable alternative to the organic solvents currently employed in nuclear fuel processing.

Notes and References

* E-mail: cwai@uidaho.edu

† Measurements were performed using high pressure fibre optic cells constructed in-house. The cells are connected in series and have path lengths of 1 cm, 733 μm and 38 μm, enabling measurements to be made over a wide concentration range. CO_2 was saturated with the complex using a high pressure view cell,[3] with a volume of 15 ml, as an equilibration vessel. Approximately 5–7 ml of $UO_2(NO_3)_2 \cdot 2TBP$ were loaded into the view cell, and, after a period of equilibration, the saturated CO_2 was introduced into the fibre optic cells and UV spectra recorded.

‡ Hexane has a similar polarity to CO_2, and UV–VIS spectra have been shown to exhibit similar absorption coefficients and negligible shifts in the positions of absorption maxima.[11] Our work has also shown that the molar absorptivity of the complex is not affected by changes in the density of the fluid. A high pressure view cell, with a path length of 5 cm and a volume of 15 ml³, was employed to determine the effect of temperature and pressure on the spectrum of the complex. An aliquot of $UO_2(NO_3)_2 \cdot 2TBP$ was placed in the cell, such that complete dissolution of the complex was achieved under supercritical conditions. Spectra were recorded over a temperature range of 40–60 °C and at pressures of 150–300 atm. No change was observed in the absorption spectrum, thus confirming the molar absorptivity is unaffected by the temperatures and pressures employed in this work.

§ The highest solubility previously reported for a metal chelate in supercritical CO_2, was chromium(III) dipivaloylmethane, $Cr(thd)_3$, with a concentration of 0.126 M at 40 °C and 310 atm.[12]

1 K. E. Laintz, C. M. Wai, C. R. Yonker and R. D. Smith, *Anal. Chem.*, 1992, **64**, 2875.
2 N. G. Smart, T. Carleson, T. Kast, A. A. Clifford, M. D. Burford and C. M. Wai, *Talanta*, 1997, **44**, 137.
3 K. E. Laintz, C. M. Wai, C. R. Yonker and R. D. Smith, *J. Supercrit. Fluids*, 1991, **4**, 194.
4 Y. Lin, R. D. Brauer, K. E. Laintz and C. M. Wai, *Anal. Chem.*, 1993, **65**, 2549.
5 Y. Lin, C. M. Wai, F. M. Jean and R. D. Brauer, *Environ. Sci. Technol.*, 1994, **28**, 1190.
6 Y. Lin, N. G. Smart and C. M. Wai, *Environ. Sci. Technol.*, 1995, **29**, 2706.
7 Y. Meguro, S. Iso, H. Takeishi and Z. Yoshida, *Radiochim. Acta*, 1996, **75**, 185.
8 N. W. Alcock, M. M. Roberts and D. Brown, *J. Chem. Soc., Dalton Trans.*, 1982, 25.
9 C. D. Auwer, C. Lecouteux, M. C. Charbonnel, C. Madic and R. Guillaumont, *Polyhedron*, 1997, **16**, 2233.
10 M. Benedict, T. H. Pigford and H. W. Levi, *Nuclear Chemical Engineering*, McGraw-Hill Book Co., New York, 2nd edn., 1981, pp. 508.
11 K. D. Bartle, A. A. Clifford, S. A. Jafar and G. F. Shilstone, *J. Phys. Chem. Ref. Data*, 1991, **20**, 713.
12 A. F. Laglante, B. N. Hansen, T. J. Bruno and R. E. Sievers, *Inorg. Chem.*, 1995, **34**, 5781.