Visible and Near-IR Spectroscopic Studies of Uranium(IV) Oxychloride in a $MgCl_2$−KCl Melt

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Although the chemistry of uranium(IV) chloride complexes in molten chloride melts has been widely investigated,[1−3] no studies of uranium(IV) oxychloride complexes in these melts have appeared, with the exception of a recent paper from our laboratory.[4] In that paper, visible and near-IR absorption bands overlapping with those of the uranium(IV) chloride complex are attributed to oxychloride species. Attempts have been made to prepare solutions containing uranium oxychloride by a direct dissolution of $UOCl_2$ into solvents such as water, acids, and molten pyridinium chloride.[5] However, only uranium(IV) chloride complex species are recovered. This led Ewing to conclude that the uranium−oxygen bond in $UOCl_2$ is stabilized only in the solid state probably by the lattice energy of the crystal.[5] Here we want to report, for the first time, the visible and near-IR spectra of uranium oxychloride in molten $MgCl_2$−KCl without interference from those of uranium(IV) chloride complexes. In addition, experimental evidence is provided to confirm that the new uranium(IV) species is an oxygen-containing chloride complex.

The preparation and purification of uranium tetrachloride and uranium oxychloride have been reported previously.[4] The UCl_4 was purified by loading the nominally pure starting material in a silica tube and pumping it down to ~20 μmHg at 650 °C to remove any moisture or HCl. The tube was then sealed, and UCl_4 was sublimed from one end of the tube to the other at 510 °C. The $UOCl_2$ was prepared by combining stoichiometric amounts of UCl_4 and Sb_2O_3 at 150 °C and then steadily raising the temperature to 300 °C, where the $SbCl_3$ byproduct distilled from the $UOCl_2$ product in a temperature gradient. The procedure for the purification of $MgCl_2$ and KCl has been described previously.[6] All molten salt solutions were prepared under a helium atmosphere in a drybox. Samples were loaded into a quartz cuvette (1-cm path length) which was then sealed under vacuum. Absorption spectra were measured from 2200 to 400 nm as a function of temperature according to the procedure described by Brynestad et al.[7] Visible and near-IR spectra were measured by a Cary 14 scanning spectrophotometer converted by On-Line Instrument Systems (OLIS) for data acquisition and analysis by an IBM-compatible computer.

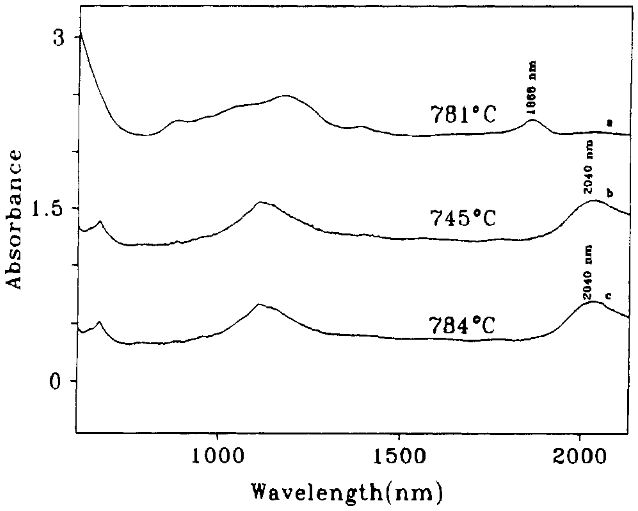

Figure 1. Visible and near-IR absorption spectra: (a) uranium oxychloride complex at 781 °C; (b) uranium chloride complex at 745 °C; (c) uranium chloride complex obtained from the reaction of the uranium oxychloride complex with CCl_4 at 784 °C in a binary melt composed of $MgCl_2$−KCl (50−50 mol %).

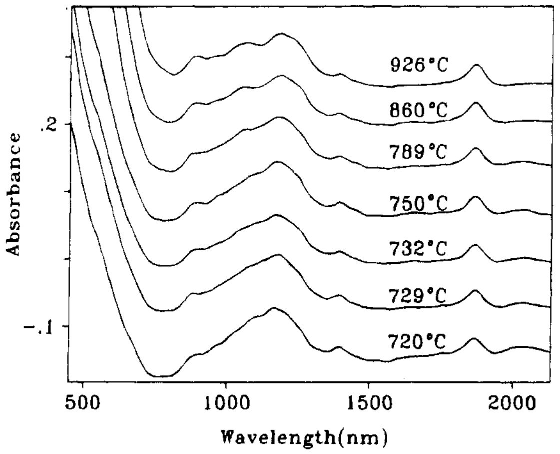

Figure 2. Variation of visible and near-IR absorption spectra of the uranium oxychloride complex in $MgCl_2$−KCl (50−50 mol %) melt with temperature.

Figure 1a gives the visible and near-IR spectrum of the uranium oxychloride complex in a $MgCl_2$−KCl (50−50 mol %) melt. This solution was obtained via the dissolution of $UOCl_2$ into the $MgCl_2$−KCl melt, followed by heating the melt for 3 h at 1000 °C to distill out the UCl_4 impurity and filtering out the undissolved $UOCl_2$ residue. The main absorptions for the oxychloride species lie at 1868, 1320, and 1230 nm. Figure 1b shows typical visible and near-IR spectra of a molten salt solution prepared by the dissolution of UCl_4 into the same melt. The similarity between the general spectral pattern of this spectrum and those recorded for UCl_4 in high-temperature $AlCl_3$−KCl melts and for $(Et_4N)_2UCl_6$ in nonaqueous organic solvents[2] strongly indicates that the same species is involved in these systems. Morrey[2] deduced the uranium chloride complex species in the KCl−$AlCl_3$ melt to be a UCl_6^{2-} species. This assignment is based on the comparison of the UV−visible spectrum of the melt with that of an authentic UCl_6^{2-} species in a solid host matrix, namely Cs_2UCl_6. As seen from Figure 1, no absorption bands are found near 1868 nm in the spectrum of uranium(IV) hexachloride complex species, whereas a strong band exists in this range of the spectrum corresponding to the melt prepared by dissolution of $UOCl_2$ in $MgCl_2$−KCl (50−50 mol %). Unlike that of UCl_6^{2-}, the near-IR spectrum of the melt prepared by dissolution of $UOCl_2$ in the $MgCl_2$−KCl (50−50 mol %) melt is virtually flat in the 2040-nm range. These prominent differences between the two spectra (Figure 1a,b) demonstrate that two different species are involved. Since Figure 1a was obtained by measuring the sample prepared via the dissolution of $UOCl_2$, it is reasonable to conclude that the corresponding species is an oxychloride complex. It is well-

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known that metal oxides can react with CCl_4 at high temperature to produce the corresponding chlorides.[8] Recently, Chen et al. demonstrated the use of CCl_4 to remove oxide impurities in molten salt media.[9] Quantitative addition of 0.05 mL of CCl_4 into the above melt gives rise to the spectrum shown in Figure 1c. Clearly, this spectrum is identical to that of UCl_6^{2-} (Figure 1b) in the same melt. This chemical test therefore establishes that the spectrum (Figure 1a) is from a uranium oxychloride species.

The temperature variation of the visible/near-IR spectra for this uranium(IV) oxychloride species is shown in Figure 2. A temperature change from 720 to 926 °C gives rise to little changes in the intensity of near-IR bands. This indicates that the volatility of uranium oxychloride is negligible in this temperature range. This behavior is in contrast to the volatility of the uranium(IV) hexachloride complex in the same melt,[10] where the chloride complex sublimes to cold spots in the form of UCl_4. Although pure solid $UOCl_2$ is known to decompose to UO_2 and volatile UCl_4 at temperatures above 800 °C,[11] the uranium(IV) oxychloride complex is stable in the melt above 800 °C, indicating that coordination of $UOCl_2$ with the solvent is probably much stronger than that of UCl_4 with the solvent.

In conclusion, visible and near-IR spectra of a uranium(IV) oxychloride species have been recorded in the absence of interference from UCl_6^{2-}. Reaction of this species with CCl_4 gives the spectra corresponding to the uranium(IV) chloride complex. The temperature variation experiment demonstrates the low volatility and high stability of the oxychloride species in the $MgCl_2$–KCl (50–50 mol %) melt.

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