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THE ABSORPTION SPECTRUM OF $UOCl_2$ IN MOLTEN CHLORIDE SALTS

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ABSTRACT

The absorption spectrum of $UOCl_2$ in molten KCl-$MgCl_2$ salts has been measured and compared with that of the related UCl_4 spectrum at temperatures up to 932°C and melt compositions of 60-40, 34-66, and 0-100 mol %, respectively, KCl-$MgCl_2$. The species $UOCl_2$ is an important intermediate in the conversion of UO_2 to UCl_4 and its spectrum provides a means of monitoring the reaction, and other similar reactions, in situ. The solubility of $UOCl_2$ has been determined from absorption spectra and has been found to be 10 to 25 times higher than reported earlier with mole fractions as high as 0.0019 in pure $MgCl_2$ at 932°C.

INTRODUCTION

The behavior of U(IV) in molten halide salts was actively studied two decades ago at a number of laboratories utilizing a wide variety of analytical techniques. Of particular interest has been the usage of absorption spectroscopy for the measurement of uranium spectra in molten chlorides (1,2) and fluorides (3,4) at temperatures up

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to 1000°C. A prime concern in the earlier studies was the spectra of uranium solutes in the *pure* halide salts; and, as a result, much effort was expended in preparing the halides free of oxide or other impurities. The findings of that era included the coordination behavior of the U(IV) solute in the halide melt. For UCl_4 in chloride melts (1), the coordination behavior of the U(IV) ion varied around a sixfold, octahedral arrangement of Cl^-, while in fluorides (3), coordination numbers of seven and eight were found—all of these changes depending measurably on the melt composition.

In a practical sense, one seldom encounters situations where pure single components are present. It is more common to find interfering components (often atmospheric) present and interacting with solution components or complicating the chemistry by introducing unwanted side reactions. Many separations processes are directed at such complexities and successful manipulation of the chemistry demands an understanding of these mixed systems.

One such example is in the separation/purification of a metallic phase which begins with an oxide form that is converted through a molten halide solution to some ultimate chemical form as has been used in the Hall-Heroult process to produce aluminum (5). During the course of this conversion, the metal ion must progress from an oxide to a mixed oxide/halide species and finally to the product. The ability to monitor the mixed oxide/halide species will often be significant in understanding and controlling such a chemical process. Even though there is often some information available on the pure oxide or the pure halide species, there is often little, if anything, available on the mixed species.

Such a case exists with U(IV) because the spectra of the pure halide-coordinated species had been characterized several years ago (1-4) and yet nothing has been reported about the oxyhalide species. Since simple coordination numbers of 6, 7, and 8 about U(VI) can be readily distinguished, it should be possible to identify spectral differences caused by the inclusion of an oxygen ligand in the first coordination sphere around the U(IV) ion, providing that the oxyhalide species is stable and its solubility is great enough that sufficient concentrations for detection could be achieved.

The concentration of $UOCl_2$ in molten LiCl-KCl at 450°C has been predicted by Chiotti et al. (6) to be at least 3.4×10^{-5} mole fraction. Molina (7) has suggested that it is as much as ten times higher in this solvent. Even with the lower concentration and a molar absorptivity equivalent to that of the pure halide, it should be possible to detect the oxychloride species in a cell of reasonable pathlength.

Therefore, we have sought to measure the absorption spectrum of U(IV) oxychloride in molten chlorides and to determine if it could be distinguished from the pure UCl_4 should the two occur together. In addition, because both of these reported solubilities are significantly lower than that of $UOCl_2$ in the $UOCl_2$-UCl_4 two-component system (8), we wanted to examine the effect of solvent composition changes on the solubility of the $UOCl_2$ species.

EXPERIMENTAL

The salt components were obtained as follows: 99.95% pure $MgCl_2$ from Anderson Physics Laboratory, Urbana, Illinois; KCl from EM Science, Cherry Hill, New Jersey; and 99.7% pure UCl_4 from Cerac, Inc., Milwaukee, Wisconsin.

For the molten salt solvent, the KCl-$MgCl_2$ mixtures were purified by sparging with a dilute Cl_2/He gas mixture at 600°C for 18 h in a graphite crucible held within a 54-mm silica tube. After treatment, the enclosed graphite crucible was moved to an inert atmosphere glove box where the contents were removed and stored for further use.

The $MgCl_2$, when used alone, was purified by loading the nominally pure starting material in a silica tube and pumping it down to ~ 20 μ Hg at 650°C to remove any moisture or HCl (as a result of hydrolysis). The tube was then sealed and the $MgCl_2$ contents distilled from one end of the tube to the other, while the hot end was held at 850°C and the other allowed to protrude from the tube furnace.

The UCl_4 was purified in a manner similar to the $MgCl_2$, but sublimed in the sealed silica tube at 510°C, instead. The $UOCl_2$ was prepared according to the method described by Bagnall et al. (9) where stoichiometric amounts of UCl_4 and Sb_2O_3 were combined in a sealed, evacuated silica tube and cooked at 150°C in a tube furnace for a period of ~ 5 h to effect the reaction:

$$3UCl_4 + Sb_2O_3 = 3UOCl_2 + 2SbCl_3. \quad (1)$$

The mixture was then heated at the reactant end to 450°C, while the other end protruded from the furnace to condense the $SbCl_3$ reaction product.

An X-ray diffraction examination of the $UOCl_2$ indicated a very microcrystalline material (weak diffraction pattern) with the 13 most prominent diffraction lines being matched with those reported for $UOCl_2$ (10). A few additional lines not associated with $UOCl_2$ were attributed to 5 to 10% of the sample as UO_2. This impurity, however, was acceptable since it would not affect the results of the spectrophotometric measurements.

A NUJOL mull of the $UOCl_2$ produced a spectrum that matched the one previously reported (9) except for a strong band at ~ 300 cm^{-1}. We have found that, on leaving the sample out in the air for a period of time, the 300-cm^{-1} band grew in and, therefore, concluded that the prominent 300-cm^{-1} band is due to a hydrolysis impurity.

Absorption spectra were measured from 2400 to 400 nm as a function of temperature and melt composition in sealed silica rectangular cuvettes (1-cm pathlength) according to the procedure described by Brynestad et al. (11). Approximately 0.05 to 0.10 g of $UOCl_2$ or UCl_4 solute were loaded along with about 5 to 8 g of solvent salt (within an inert atmosphere glove box of <1 ppm moisture) into a silica tube which had been fused to the top of the 1-cm cuvette. The tube was then attached to a vacuum manifold, evacuated, filled with 1/3 atm of dry helium, and sealed off with a torch. This sealed cell containing the sample was placed in an optical furnace, heated to melt temperatures, and the spectra recorded at various temperatures on a Cary 14H or 17H recording spectrometer. Baseline/solvent salt spectra were recorded similarly and digitally subtracted from the sample spectra. On some occasions a smoothing routine was used to reduce the noise level of the spectra presented.

RESULTS AND DISCUSSION

Spectrum of $UOCl_2$

The KCl-$MgCl_2$ mixtures used as the molten-salt solvent not only provided a relatively low-melting mixture in some proportions but also permitted control of the chloride-ion activity across the range of compositions from pure KCl to pure $MgCl_2$. The phase diagram of the KCl-$MgCl_2$ system has been reported previously (12) and was used to guide the selection of the melt compositions. Initially, relatively high Cl^- activities were desired [as would be expected in the KCl-$MgCl_2$ (60-40 mol %) composition]; but, as the work developed, more acidic (i.e., Cl^- deficient) solvents were used. This variation in melt composition was used mainly to determine the affect of Cl^- activity on $UOCl_2$ solubility so that some comparison might be made between solubilities reported in basic solvents and those expected in acidic media such as pure $MgCl_2$ or UCl_4.

The spectra of $UOCl_2$ and UCl_4 at 930°C in KCl-$MgCl_2$ (60-40 mol %) and (34-66 mol %) are shown in Figs. 1 and 2, respectively. Absorbances shown are for the $UOCl_2$ solute, while the intensity of the UCl_4 band was adjusted by a factor of ~0.2 to be equivalent to that of the $UOCl_2$. The affect of temperature on the absorption spectrum of $UOCl_2$ in KCl-$MgCl_2$ (34-66 mol %) is shown in Fig. 3.

The spectra of UCl_4 in these melts are similar to those which have been reported previously (1-3). Especially pertinent are the changes cited by Morrey (1) as a function of melt composition which are indicative of changes in the U(IV) speciation. Although Morrey did not stress any significance about the weak 1800-nm band, we have observed the appearance of this band in both our UCl_4 spectra of Figs. 1 and 2 and Morrey's spectra for the acidic melts of pure UCl_4 and UCl_4 in $ZnCl_2$. More will be addressed regarding this band in the discussion of $UOCl_2$.

While the spectra of $UOCl_2$ in the KCl-$MgCl_2$ melts are similar in many respects to those observed for UCl_4 [as they should be for these f→f transitions on the U(IV) in these environments], there are several features which are distinctly different, especially the intensity of the 870- and 1872-nm bands which grow with increasing temperature and $MgCl_2$ content. In the acidic limit (i.e., pure $MgCl_2$) the 1872-nm band is very intense and an additional band at 1514 nm appears; these two bands increase and decrease, respectively, with increasing temperature, as seen in Fig. 4. Meanwhile, the intensity of the bands in the 1000- to 1200-nm range remains relatively constant.

As indicated earlier, changes such as these identified (1) with UCl_4 were attributed to changes in the various U(IV) species occurring as a result of

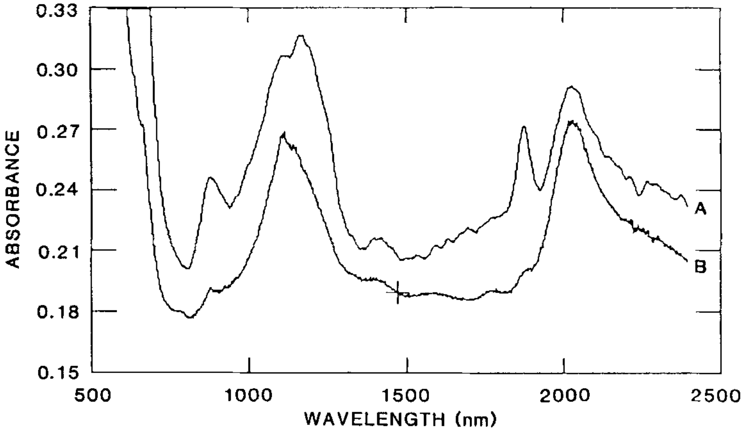

FIGURE 1. Absorption spectra of (A) $UOCl_2$ and (B) UCl_4 at 930°C in molten KCl-$MgCl_2$ (60-40 mol %). The UCl_4 absorbance has been reduced by a factor of 0.2 to scale with the $UOCl_2$.

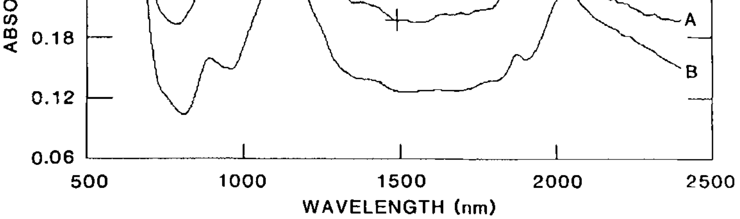

FIGURE 2. Absorption spectra of (A) $UOCl_2$ and B) UCl_4 at 930°C in molten KCl-$MgCl_2$ (34-66 mol %). The UCl_4 absorbance has been reduced by a factor of 0.2 to scale with the $UOCl_2$.

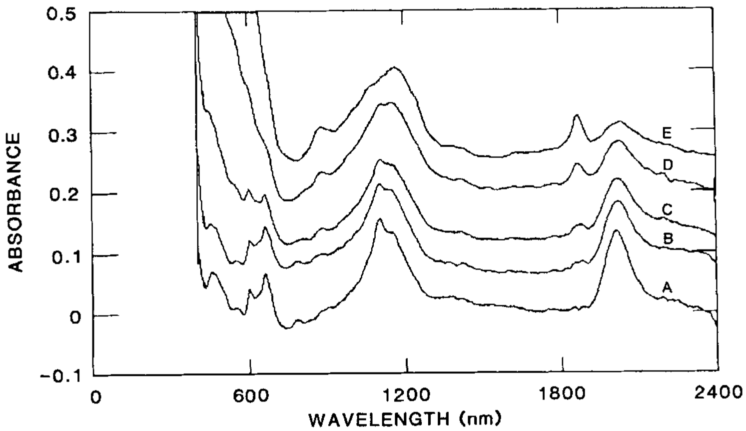

FIGURE 3. Absorption spectra of UOCl$_2$ in molten KCl-MgCl$_2$ (34-66 mol %) at (A) 542°, (B) 635°, (C) 716°, (D) 820°, and (E) 932°C.

coordination with the solvent components. Similarly, these spectral changes for UOCl$_2$ caused by variations in the solvent composition are attributed to changes in the nature of the coordination behavior about UOCl$_2$. In contrast to the UCl$_4$ solute which produced the UCl$_6^=$ species of high symmetry, O$_h$, and corresponding low absorptivity, UOCl$_2$ must exist as species of considerably lower symmetry and thus should not show such dramatic changes in molar absorptivity as the solvent is varied.

It has been noted (13) that bands 1390 and 1872 nm are very close to OH$^-$ combination and overtones which could enter the system through a moisture-contaminated MgCl$_2$ solvent. We have not been successful in demonstrating (through infrared spectra) that the solvent or the sample itself contained any moisture during the course of the experiment. Furthermore, the expected instability of the OH$^-$ species at temperatures >900°C to form HCl and the corresponding oxide lends doubt about the assignment of these bands to OH-related vibrational bands. Consequently, the two prominent bands at 1514 and 1872 nm are assigned to electronic bands of the UOCl$_2$ species in solution.

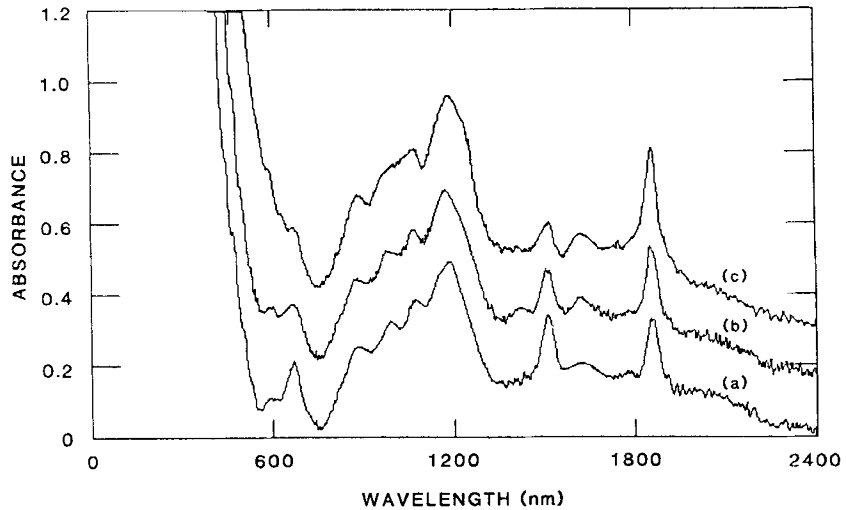

FIGURE 4. Absorption spectrum of $UOCl_2$ in molten $MgCl_2$ at (a) 744°, (b) 823°, and (c) 936°C.

Solubility of $UOCl_2$

With the UCl_4 solute, complete dissolution was achieved upon melting to yield homogeneous solutions. The molar absorptivities of UCl_4 in solutions such as these could then be simply determined from the absorbance measurements. However, when $UOCl_2$ was the added solute, only a fraction of it dissolved. It is this limited solubility of $UOCl_2$ that largely controls the oxide capacity of the melt. Therefore, an attempt was made to determine the solubility of $UOCl_2$ through the spectroscopic measurements.

From the results of the spectral measurements discussed earlier, the molar absorptivity of $UOCl_2$ was chosen to be the same as that for UCl_4 under similar melt conditions with the realization that the molar absorptivity of UCl_4—in situations of low coordination symmetry—does not change significantly in going from the chloride to the fluoride salts. (This is evident from the values calculated from this work and those data given in Ref. 3.) Furthermore, in the KCl-$MgCl_2$ solvent system here (as was the case in the fluoride melts) (3), there was little spectral evidence for the occurrence

TABLE 1. SOLUBILITY OF $UOCL_2$ EXPRESSED AS MOLAR CONCENTRATIONS AND MOLE FRACTIONS AFTER SATURATING MOLTEN SALTS AT 932°C AND ESTIMATING CONCENTRATIONS FROM THE INTENSITY OF THE 1100- TO 1200-NM ABSORPTION BAND OF $UOCl_2$

Solvent KCl-$MgCl_2$ (mol %)	Molar Concentration (mol/L)	Mole Fraction
60-40	0.015	8.9×10^{-4}
34-66	0.014	7.5×10^{-4}
0-100	0.036	1.9×10^{-3}

of the centrosymmetric $UCl_6^{=}$ species of unusually low molar absorptivity as identified by Morrey (1); and, consequently, the absorptivities for the uranium chloride species in this system appear to be very comparable. A similar situation should exist for the $UOCl_2$ solute since it cannot form species which are highly centrosymmetric, and thus it should have an absorptivity that is comparable to that found for UCl_4 in the low-symmetry situations. The maximum absorptivity values for the f→f transitions of these species in halide melts have been previously found (3) to be of the order of 10 to 20 $\underline{M}^{-1}cm^{-1}$. An average value of 12.3 $\underline{M}^{-1}cm^{-1}$ was measured for UCl_4 and used for $UOCl_2$ in the KCl-$MgCl_2$ solvent system.

Table 1 gives the molar concentrations and mole fractions which were determined for $UOCl_2$ at 932°C. There was little effect of temperature on this solubility, as indicated by the rather constant intensity of the bands shown in Fig. 3. Although the uncertainty in the solubility measurement is estimated to be ±0.005 $\underline{M}$, it is clear from these data that the solubility of $UOCl_2$ increases significantly in going from the KCl-$MgCl_2$ solvent mixtures to that of pure $MgCl_2$. This increase in solubility has been previously noted in the Th(IV) system(6) and has been attributed to the reaction:

$$MgCl_2 + ThO_2 \rightarrow ThOCl_2 + MgO, \qquad (2)$$

for which the standard free energy change is -12.1 kcal at 700°C. However, it is apparent in our work that the greater solubility of $UOCl_2$ in $MgCl_2$ is like that in pure UCl_4 and is due to the solvating effect of an acidic solvent species which is halogen bridged to the uranium atom of $UOCl_2$.

This halide bridging has been recognized in the case of $AlCl_3$ complexes with transition metal chlorides (14) where, by sharing chloride ligands, $AlCl_3$ satisfies its coordination requirements and those of the transition metal ion which would both otherwise be deficient in coordinating ligands.

The bonding through the chloride bridge from the $MgCl_2$ to the uranium metal atom would then produce $(MgCl_2)_xUOCl_2$, where $x = 1$ or 2, in solution. Even though there was some UO_2 impurity indicated from the X-ray analysis of our $UOCl_2$, varying amounts of added solute (with the associated increase in the available UO_2 impurity) produced no increase in the amount of $UOCl_2$ found in solution. This observation gave support to our understanding that the reaction given in Eq. 2 was not taking place here. Rather, the solubility behavior in these molten chlorides appears to be simply the solvation effects that occur in varying acid/base properties of the solvent. In a similar fashion, the higher solubility of $UOCl_2$ in UCl_4 as shown by the UO_2-UCl_4 phase diagram (8) would be due to the bridging effect of one or more UCl_4 species to form $(UCl_4)_xUOCl_2$.

The solubility measured for $UOCl_2$ is more than 10 times that found by Chiotti et al. (6) in a similar solvent system (NaCl-$MgCl_2$); and, for the pure $MgCl_2$ solvent (realizing that they did not look at a solvent this acidic), it is more than 25 times that reported by them. These authors acknowledge (6) "that the $ThCl_4$-$ThOCl_2$ system shows that at the eutectic temperature, 715°C, solid $ThOCl_2$ is in equilibrium with liquid salt containing 26 mol % $ThOCl_2$" but do not seem to recognize that the large amount of Th(IV) oxychloride in solution is due to the solvating effect of the acidic $ThCl_4$. The greater solubility of both of these oxychlorides, Th(IV) and U(IV), in the pure metal chloride is easily understood as the limiting case in the solvation effects as described above and consistent with the trends in solubility observed as the composition of the melt is changed.

CONCLUSIONS

The absorption spectrum of $UOCl_2$ in molten chloride solutions of varying acidity has been shown to vary as the free chloride content of the melt is changed. However, there is little change in the intensity of the spectrum with temperature and coordination changes. From the corresponding behavior of UCl_4 in these melts, it is apparent that the species present both as pure chloride and as the oxychloride are not of high symmetry and therefore should have intensities which are comparable to those seen in other halide melts of similar properties. Nevertheless, features in the near-IR region of the $UOCl_2$ clearly distinguish it from the UCl_4 analog; this is especially evident at 1872 nm where an ideal absorption band for analytical purposes can be found.

By using the value of UCl_4 molar absorptivity to determine the solubility of $UOCl_2$, it is found that the solubility is approximately 10 to 25 times greater than that measured previously. In order for these measured solubilities to correspond to those measured previously, it would be necessary for the $UOCl_2$ molar absorptivity to be 10 to 25 times greater than that of UCl_4 in the same melt. This is not viewed as a plausible situation since the $UOCl_2$ absorptivities would have to be 100 to 300 $M^{-1}cm^{-1}$ —values which are far too large for $f \rightarrow f$ transitions of this nature. Finally, the higher $UOCl_2$ solubility found here are consistent with the solvation effects understood for acidic solvent components, such as $MgCl_2$, $AlCl_3$, and UCl_4, and these solubility trends are substantiated in the limit by the high concentration of oxychloride in the UCl_4 region of the UO_2 to UCl_4 phase diagram.

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