shortening of the Cl–O bond in the series ClO_2^-, ClO_3^-, and ClO_4^- [12] and the increasing Cl–O stretching force constant[13] have been attributed to the increasing π bonding. Comparable bond-length data are not available for the BrO_n^- series. In an attempt to explain the instability of BrO_4^-, Urch[14] has attempted to calculate the relative efficiencies of the chlorine 3d and the bromine 4d orbitals in their π bonding with oxygen 2p orbitals and has concluded that the 4d orbitals are much less efficient. Since the tetrahedral σ-bond frameworks for these XO_4^- ions are similar and weak, because the 3s and 4s electrons are tightly bound and cannot participate effectively, he further concludes that the absence of good π bonding in BrO_4^- explains its instability. The present correlation suggests, however, that, if increasing π bonding is the predominant factor in the ClO_n^- series, it is probably also this factor which predominates in producing the analogous changes in bond force constants in the BrO_n^- series; *i.e.*, 3d–2p and 4d–2p π bonding are not very different in efficiency, at least in the first three members of the series.

CONTRIBUTION FROM THE ANALYTICAL CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE

Spectra of Uranium(IV) and Uranium(III) in Molten Fluoride Solvents[1]

BY J. P. YOUNG

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The spectra of U(IV) and U(III) in molten $LiF–BeF_2$, $LiF–BeF_2–ZrF_4$, and LiF–NaF–KF have been obtained at temperatures up to 540° over the wavelength range of 200 to 2400 nm. Based on a comparison of these spectra with those obtained in other molten salt systems and aqueous systems, it is suggested that the coordination number of the uranium species in the molten fluoride media studied is possibly 8 or 9. Clearly, these ions are not in the environment found in chloride melts. By chemical means, it was not possible to obtain a solution of U(III) which was free of U(IV). The reaction of U(III) with alkali fluorides, under the experimental conditions of the study, is also discussed.

Introduction

Spectrophotometry offers a rather straightforward approach to the determination of various oxidation states of uranium in molten fluoride salts provided the effect of various parameters on the spectra of these dissolved species is known. A study of the spectra of U(IV) and U(III) in several molten fluoride solvent systems was undertaken in order to gain knowledge about the environment of these solute species and compare this environment to that of other solvent systems. Earlier the partial spectrum of uranium(IV) in molten LiF–NaF–KF had been reported.[2] The work described here was carried out mainly in the solvent systems $2LiF–BeF_2$ (66–34 mole %), $LiF–BeF_2–ZrF_4$ (66–29–5 mole %), and LiF–NaF–KF (46.5–11.5–42.0 mole %). Spectra of U(IV) and U(III) in various molten chloride solutions have been reported by Gruen and McBeth[3a] and by Morrey.[3b]

Experimental Section

These spectra were recorded by means of a Cary recording spectrophotometer, Model 14M. The molten LiF–NaF–KF samples were contained in 0.25-in. o.d. captive liquid cells[4] and the molten samples of the $LiF–BeF_2$ type were contained in modified captive liquid cells which had no "keeper holes."[4] As $LiF–BeF_2$-type melts are nonwetting, the keeper holes are unnecessary. In a further modification to reduce the volume of salt required, the optical apertures were located about $^1/_{32}$ in. above the bottom of the cell. The cells were made of copper or graphite for these studies. They were loaded with solid chunks of solidified salt solutions, chunks of solidified solvent, and solid UF_3 or UF_4 which would dissolve on melting, or with solvent and UF_4 plus a reducing agent such as uranium, zirconium, or beryllium metal. In all cases, the samples were loaded in an inert atmosphere box. Each loaded cell was placed in a vacuum-tight container for transfer to the heated cell assembly without exposure to the atmosphere as the transfer container served as the lid of the cell assembly. The cell is suspended[4] on a quartz rod, and the end of the rod protrudes through a Teflon ferrule in the top of the transfer container. After the cell assembly had been evacuated and filled with helium gas, a modified gate valve was opened in the bottom of the transfer container and the captive liquid cell and its contents were lowered and positioned within the cell assembly by manipulation of the portion of the quartz rod which was outside the furnace. Generally the cell assembly and its contents are baked under vacuum at 250° for 1 hr before helium is readmitted and the sample melted.

The samples were melted in a heated cell assembly similar in external appearance to the one described earlier[5] but modified internally so that the sample and cell are contained in a vacuum-tight helium atmosphere. The interior of the cell assembly consists of an inverted T-shaped nickel tube. Light from the spectrophotometer passes through the horizontal portion of the "T" which is welded to the exterior walls of the cell assembly. The vertical part is welded to the top of the assembly. Windows are sealed on the cooled ends of the horizontal tube as described before.[5] Ten rod-shaped heating elements are positioned outside the junction of the "T" but within a large mass of nickel which surrounds the junction; thus, the mass of heated metal provides more uniform heating than that of the original design. Further,

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[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

[2] J. P. Young and J. C. White, *Anal. Chem.*, **32**, 799 (1960).

[3] (a) D. M. Gruen and R. L. McBeth, *J. Inorg. Nucl. Chem.*, **9**, 290 (1959); (b) J. R. Morrey, *Inorg. Chem.*, **2**, 163 (1963).

[4] J. P. Young, *Anal. Chem.*, **36**, 390 (1964).

[5] J. P. Young and J. C. White, *ibid.*, **31**, 1892 (1959).

the heating elements and auxiliary insulation are located outside the sample cavity so that the atmosphere of the sample cavity cannot be contaminated by gaseous products from such materials. A photograph of the modified cell assembly and further details of construction are available.[6]

The solvents LiF–NaF–KF, 2LiF–BeF$_2$, and LiF–BeF–ZrF$_4$ were prepared by standard methods.[7] After spectral study the samples were rapidly quenched and the solid sample was analyzed for uranium content. In some instances, various portions of the solidified sample were analyzed separately to verify complete dissolution of the solute or to eliminate errors due to a precipitate or excess metal.

Results

The spectrum of U(IV) over the wavelength range of 200 to 1500 nm in molten LiF–BeF$_2$ is shown in Figure 1. Within the limits of the measurement, there are no further absorption peaks in the wavelength region of 1500 to 2400 nm. Not shown in the figure is the ultraviolet spectrum of U(IV) in LiF–NaF–KF, which is similar in shape except that the shoulder is shifted to 250 nm. The spectrum of U(III) in LiF–BeF$_2$ over a similar wavelength range is shown as the solid line curve in Figure 2. A further weak and broad absorption was noted at 2070 nm (molar absorptivity *ca.* 5) but was not characterized further. The spectrum of U(III) in molten LiF–NaF–KF is the dashed line curve in Figure 2. Trivalent uranium is unstable in the alkali fluoride solvent, under the conditions of the experiment, with respect to oxidation *via*

$$\mathrm{U(III)} + \begin{pmatrix}\mathrm{Na}^+\\ \mathrm{K}^+\end{pmatrix} \longrightarrow \mathrm{U(IV)} + \begin{pmatrix}\mathrm{Na}^0\\ \mathrm{K}^0\end{pmatrix}\uparrow$$

Indeed, the resonance absorption spectra of Na and K vapor are seen superimposed on the uranium spectrum, and the spectrum of U(IV) slowly grows into the melt. The spectrum of U(III) and alkali metal vapor is observed if either UF$_3$ or simply uranium metal is added to the solvent. This reaction is not favored thermodynamically but probably proceeds by distillation of the alkali metals to the water-cooled exterior portions of the furnace. The resonance absorption spectrum of lithium metal vapor is not observed either in the alkali fluoride or the BeF$_2$-type melts.

In both figures, molar absorptivities are given as the ordinate. A path length of 0.7 cm was used in these calculations. This value is based on a measurement of the path length in the captive liquid cell of solidified samples of nonwetting LiF–BeF$_2$ corrected for volume expansion on melting. Due to the above estimation of path length, the molar absorptivities for U(IV) are only considered accurate to within 10%. Because of the chemical instability of U(III) in LiF–NaF–KF and the overlap of the very sensitive U(IV) and U(III) ultraviolet absorptions, the accuracy of molar absorptivities in these cases should be somewhat poorer.

Discussion

The spectrum of U(IV) in molten LiF–BeF$_2$ or LiF–BeF$_2$–ZrF$_4$ in the wavelength range of 400 to 1400 nm is very similar to the spectrum of U(IV) in LiF–NaF–KF[2] with respect to peak positions and sensitivities over the temperature range studied. About the only difference in the two is the poorer resolution of the individual absorptions which make up the absorption envelope in the 400 to 550 nm region in the BeF$_2$ melts. As seen in Figure 1, a very strong absorption is found for U(IV) at 235 nm which is on the low-energy side of an even more intense absorption. In LiF–NaF–KF the shoulder is at 250 nm. This portion of the U(IV) spectrum has not been observed previously in any molten salt system, but it corresponds well with the ultraviolet spectrum of U(IV) in 1.0 *M* DClO$_4$ discussed by Cohen and Carnall.[8] The band is shifted and reduced in intensity to that observed in DClO$_4$; the increase in temperature could partially account for this shift. Because of the shift to lower energies in the molten salt, the much weaker absorption peak reported at 245 nm[8] was not observed in the present study. The very intense ultraviolet absorptions in the U(IV) spectrum result from LaPorte-allowed transitions of the type 5f^2–5f6d,[8] where the other, and much weaker, absorptions at lower energies are transitions within the 5f orbital. These latter internal transitions tend to be much less affected by solution environment,[3a,8] although Morrey[3b] has shown that these

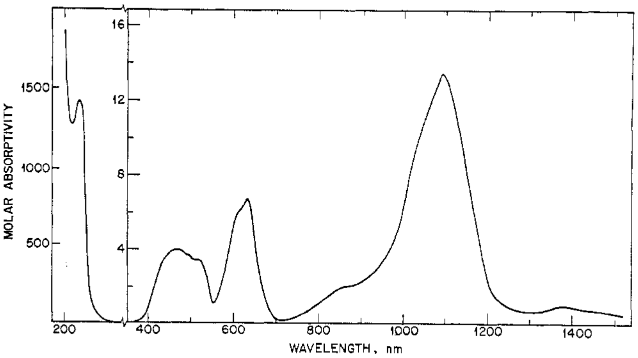

Figure 1.—Spectrum of U(IV) in molten LiF–BeF$_2$ (66–34 mole %) at 550°.

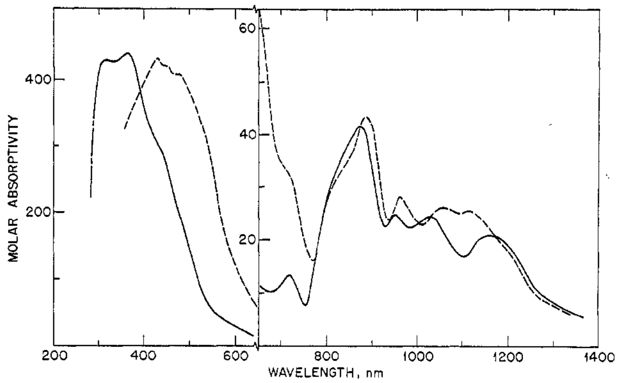

Figure 2.—Spectra of U(III) in molten fluoride solutions: – – –, LiF–NaF–KF (46.5–11.5–42.0 mole %, 525°); ——, LiF–BeF$_2$ (66–34 mole %, 550°).

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[6] Oak Ridge National Laboratory Analytical Chemistry Division Annual Progress Report, ORNL-3537, Nov 15, 1963, p 26.

[7] W. R. Grimes, D. R. Cuneo, F. F. Blankenship, G. W. Keilholtz, H. F. Poppendick, and M. T. Robinson, "Fluid Fuel Reactors," J. A. Lane, H. J. MacPherson, and F. Moslam, Ed., Addison-Wesley, Reading, Mass., 1958, p 584.

[8] D. Cohen and W. T. Carnall, *J. Phys. Chem.*, **64**, 1933 (1960).

absorptions are ineed not independent of environment. Shifts in the ultraviolet spectrum of U(IV) are apparent, however, in comparing the data of chloride melts[3] with the data in 1.0 *M* $DClO_4$[8] and the present work in fluoride melts. The similarity of the U(IV) ultraviolet spectra in the aqueous and $LiF-BeF_2$ media suggests a similar environment and one that is different from the environment existing in any chloride melt. It would be of interest to know whether this correlation is due to the similar electronegativity of fluoride and aqueous ligands or due to a similar coordination. The spectrum of U(IV) in fluoride melts is similar to the portion of the spectrum given for U(IV) in aqueous 11.8 *M* NH_4F solutions by Penneman, *et al.*[9] It is stated[9] that this aqueous spectrum is quite similar to the spectrum of solid $(NH_4)_4UF_8$ and may represent a high coordination number, possibly 8. It would seem reasonable to assume from the spectrum of U(IV) in fluoride melts, then, that a similar coordination exists. Such eightfold coordination would also be in line with the possible coordination of U(IV) in aqueous solutions. In many of the chloride melts studied, U(IV) is seen to exhibit a coordination number of 6 or less.[3]

The spectra of U(III) in the two molten fluoride media shown in Figure 2 again bear out the comparative influence of environment on probable f–d transitions[10] in the visible-ultraviolet region, and on the shielded f–f transitions at lower energies. Visually, very dilute solutions of U(III) in $LiF-BeF_2$ are yellow where U(III) in LiF–NaF–KF is red. Dilute solutions of U(III) in LiCl–KCl are reddish purple; the spectrum of U(III) in this latter solvent exhibits intense absorption in the region of 450 to 600 nm.[3a] The f–f transitions in the two mentioned fluoride melts and in the chloride melt appear to be, however, similar in intensity and position. The positions of the various f–d transitions of U(III) in $LiF-BeF_2$ are very similar to that of U(III) in 1.0 *M* $DClO_4$[8] or even 0–6 *M* HCl;[10] the intensities of the absorption envelopes are much lower in the molten fluoride solution, however. No adequate explanation of the difference in intensity can presently be offered. If one assumes that the strong absorption band for U(III) between 500 and 600 nm in molten LiCl–KCl is evidence for the existence of chloro complexes,[3a] analogous fluoro complexes do not exist in molten $LiF-BeF_2$. The case for U(III) in LiF–NaF–KF is not so clear, but the shifts noted may represent the differences in an environment in which the solvent contains weakly and more strongly bound fluoride ions.

The results of this spectral investigation suggest that in solutions of essentially $2LiF-BeF_2$ or of alkali fluorides at temperatures to 550° both U(IV) and U(III) exist in an environment quite similar to that of these ions in "noncomplexing" media such as 1.0 *M* $DClO_4$. Ryan and Jørgensen[11] suggest that this environment may represent a coordination number of 8 or 9 in 1.0 *M* $DClO_4$. These ions are not in the environment which is found in chloride melts.

As is the case in other solvent systems,[8,10] U(IV) was present in solutions containing U(III) and caused interference in the ultraviolet portion of the U(III) spectrum. In the fluoride melts studied, it was not possible by chemical means to preferentially eliminate the higher oxidation state. In spectral studies of the dissolution of solid UF_3 in molten $LiF-BeF_2$ the first absorption to appear, and grow in intensity, was the 235 nm peak of U(IV). Later, the spectrum of U(III) appeared. It cannot be known for certain whether the U(IV) was formed chemically by reaction of U(III) with some unknown contaminant in the melt or whether there was preferential dissolution of possible UF_4 impurity in the UF_3. It should be remembered also that the U(IV) ultraviolet spectrum is some three times more sensitive than that of U(III). The addition of uranium metal to this melt, or the dissolution of UF_3 in the presence of uranium metal, would improve the ratio of U(III) to U(IV) but not eliminate U(IV). Under the experimental conditions the addition of beryllium metal to the system decreased the concentration of both oxidation states, ultimately leading to a solution in which the U(III) concentration was below spectral detection limits but containing ~5 ppm U(IV); these particular experiments were performed in graphite captive liquid cells. Because of these problems, the portion of the spectrum of U(III) in $LiF-BeF_2$ below ~300 nm is shown as a broken curve. The instability of U(III) with respect to U(IV) is greater in the alkali fluoride melts, so the spectrum of U(III) could not be studied at all below 300 nm.

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(10) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 1503 (1956).

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