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Studies of the Ammonium Fluoride–Uranium Tetrafluoride–Water System. Properties of $(NH_4)_4UF_8$, $(NH_4)_2UF_6$, $7NH_4F \cdot 6UF_4$, and of U(IV) in Aqueous NH_4F[1]

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Emerald-green $(NH_4)_4UF_8$ is the solid phase in equilibrium at 25° with aqueous solutions containing from 24.2 wt. % NH_4F to 45.1 wt. % (saturated) NH_4F. Its solubility in this range is given in terms of molalities by $[U(IV)] = 655[NH_4F]^{-5} + 0.00465[NH_4F]^{1/2}$. From solutions less concentrated than 24.2 wt. % NH_4F, the lower complexes $(NH_4)_2UF_6$ and $7NH_4F \cdot 6UF_4$ are obtained, but $(NH_4)_3UF_7$ is not observed. $(NH_4)_2UF_6$ is polymorphic, exhibiting four crystalline modifications near room temperature. The form in equilibrium with NH_4F solutions at 25° is orthorhombic γ-$(NH_4)_2UF_6$, space group $Pmc2_1$ or Pmcm, $a_0 = 4.05$, $b_0 = 7.03$, $c_0 = 11.76$ Å., $Z = 2$. The visible spectra of U(IV) in solution show marked changes with the NH_4F concentration and some sensitivity to the U(IV) concentration. Fluoride-form anion exchanger absorbs up to 0.60 mole of UF_4 per equivalent of exchange capacity.

Introduction

Fluoride ion in high concentration stabilizes markedly the tetravalent states of americium and curium in aqueous solution,[2–4] undoubtedly through formation of fluoride complexes. Their uncomplexed M^{+4} states are unstable with respect to their M^{+3} states by more than 2.5 volts. Formation of fluoride complexes is observed with other actinide tetrafluorides, *e.g.*, ThF_4, PaF_4,[5] UF_4, NpF_4,[6] and PuF_4,[7] which are typically sparingly soluble in aqueous HF but dissolve to the extent of several g./l. in 13 *M* NH_4F. Thus, formation of soluble M(IV)–fluoride complexes occurs generally throughout the first half of the 5f series (Th–Cm) and undoubtedly would be observed with Bk(IV). The nature of the solutions and the compounds obtainable therefrom have not been investigated previously in detail.

Our interest in the NH_4F–UF_4–H_2O system was stimulated originally by attempts to prepare a U(IV) compound isostructural with the then unidentified compound $(NH_4)_4AmF_8$.[3] The present work includes study of the crystallographic properties and spectra of several ammonium uranium(IV) fluorides, as well as the solution properties of $(NH_4)_4UF_8$ including solubility. An earlier paper from this laboratory describes the anhydrous preparation and thermal analysis of ammonium uranium(IV) fluorides. In that work, $(NH_4)_4UF_8$ and $(NH_4)_2UF_6$ were obtained only in the form of fine powders whose X-ray powder patterns were complex and not indexed.[8] In the present study both were obtained as sufficiently large crystals to permit study by optical and single crystal X-ray techniques.

In the thermal analysis study,[8] the compound $(NH_4)_3UF_7$ was not found between $(NH_4)_4UF_8$ and $(NH_4)_2UF_6$ even though it was expected in analogy to the compound Rb_3UF_7,[9] since the ionic radii of Rb^+ and NH_4^+ are nearly identical. In the present solution work, therefore, a careful search was made for it.

The electromigration of Pu(IV) was studied by earlier workers,[10] who interpreted their results as indicating a negligible fraction of anionic Pu(IV)–fluoride species was present in 10.7 *M* NH_4F solution. On the other hand, Savage and Browne[11] found it necessary to

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] L. B. Asprey and R. A. Penneman, *J. Am. Chem. Soc.*, **83**, 2200 (1961).

[3] L. B. Asprey and R. A. Penneman, *Inorg. Chem.*, **1**, 134 (1962).

[4] T. K. Keenan, *J. Am. Chem. Soc.*, **83**, 3719 (1961).

[5] M. Haissinsky, R. Muxart, and H. Arapaki, *Bull. Soc. Chim. France*, 2248 (1961).

[6] T. K. Keenan, private communication, Los Alamos Scientific Lab., 1963.

[7] D. F. Bowersox, private communication, Los Alamos Scientific Lab., 1962.

[8] R. Benz, R. M. Douglass, F. H. Kruse, and R. A. Penneman, *Inorg. Chem.*, **2**, 799 (1963).

[9] R. E. Thoma, H. Insley, B. S. Landau, H. A. Friedman, and W. R. Grimes, *J. Am. Ceram. Soc.*, **41**, 538 (1958).

[10] G. T. Seaborg, J. J. Katz, and W. M. Manning, "The Transuranium Elements," IV-14B Pt. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 358.

[11] A. W. Savage, Jr., and J. C. Browne, *J. Am. Chem. Soc.*, **82**, 4817 (1960).

postulate the anionic species UF_5^- and UF_6^{-2} to explain their measurements of UF_4 solubility even in very dilute fluoride solutions. In the present work, we attempted to develop specific evidence concerning the presence of U(IV)–fluoride anions by studies of spectra, by measuring the solubility of $(NH_4)_4UF_8$ as a function of NH_4F concentration, and by a new technique involving absorption of UF_4 on fluoride-form anion resin.

Experimental

Materials and Equipment.—Two types of UF_4 were used. The first and less reactive material was prepared by hydrogen reduction of uranium hexafluoride; the second was prepared by dehydration of $UF_4 \cdot 2.5H_2O$.[12] The latter preparation yields UF_4 of high surface area which dissolves comparatively rapidly in aqueous NH_4F. Other materials were of reagent grade or equivalent and were used without further purification.

Absorption spectra were obtained using a Cary Model 14MR spectrophotometer. X-Ray powder patterns were obtained using a Debye-Scherrer 114.6-mm. powder camera and Illford G film. Single crystal studies were carried out with a Buerger precession camera. Optical studies were made using a Zeiss polarizing microscope.

General Preparative and Analytical Procedures.—The salts obtained from solutions of U(IV) in aqueous NH_4F are anhydrous and of the general formula $xNH_4F \cdot yUF_4$. Heating NH_4F and UF_4 (in the *absence* of water) yields this same series of salts as fine powders.[8] From NH_4F solution, however, well formed crystals (0.1–0.5 mm.) can be obtained. The lower members are prepared readily by treatment of the highest member, $4NH_4F \cdot UF_4$, with appropriate concentrations of aqueous NH_4F as described below. These salts may also be precipitated by addition of methanol or by cooling solutions saturated with respect to U(IV). Use of glass vessels should be avoided; either polyethylene or polyfluoroethylene containers are satisfactory.

During development of preparative methods, the salts were identified routinely by their X-ray powder patterns and visible spectra. Their identity with salts prepared by anhydrous methods[8] was confirmed by chemical analysis for U, NH_4, and F using pyrohydrolysis in superheated steam at 1000°. The residue was weighed as U_3O_8. The condensate containing NH_4F and HF was titrated to the methyl red end point, then passed through H^+-form ion-exchange resin and titrated to the phenolphthalein end point. Further details of the development and tests of this procedure are given in ref. 8.

All NH_4F solutions were prepared from a concentrated stock solution analyzed by ion-exchange techniques. Thorough pretreatment of the resin (Dowex-50) with NH_4F before conversion to H^+-form was found essential. The ion-exchange columns were drilled from clear blocks of plastic (Lucite). The resin bed was supported on Teflon felt.

Preparation of $(NH_4)_4UF_8$.—Emerald-green crystals of this salt appeared upon treatment at 25° of UF_4 with air-free concentrated NH_4F solutions. A typical preparation contained 120 g. of H_2O, 80 g. of NH_4F, and 5 g. of UF_4. Initially, the mixture became warm and a cement-like cake of dark blue $(NH_4)_2UF_6$ formed; this was broken up with a plastic rod and the bottle was rotated at 25° for 72 hr. The solid phase then consisted of well-formed green crystals which were dried on a frit and transferred to a storage bottle. When kept bottled, no change was noted after several months. Conversion into blue-green $(NH_4)_2UF_6$ was observed when the crystals were exposed for many days in a ventilated hood or *in vacuo* at 92° overnight. Measurements of the range of stability (7.07 *M* to saturated NH_4F) and solubility of $(NH_4)_4UF_8$ are described in later sections.

Preparation of $(NH_4)_2UF_6$.—The salt obtained from 3–7 *M* NH_4F at 25° has the stoichiometry $2NH_4F \cdot UF_4$. In contrast with the behavior of either $4NH_4F \cdot UF_4$ or $7NH_4F \cdot 6UF_4$, the visible spectra and X-ray powder patterns of different preparations of the 2:1 salt exhibited pronounced differences. However, no corresponding differences in composition were indicated by direct analysis. Correlation of the spectra and X-ray powder patterns for several dozen preparations established the occurrence of four crystalline modifications of $(NH_4)_2UF_6$ designated here as the α-, β-, γ-, and δ-forms.

The equilibrium form at 25° in 6.4 *M* NH_4F is the γ-form. This was established by approaching the equilibrium from both directions. Samples prepared by addition of UF_4 and of $(NH_4)_4UF_8$ to NH_4F solutions containing 21.9% by weight NH_4F at equilibrium were rotated for 6 weeks at 25°. The spectra of the solids became constant within 5 days. The equilibrium solid phase in each experiment was identified as γ-$(NH_4)_2UF_6$ by its visible spectrum and X-ray powder pattern. No studies of equilibria involving the other forms were made; however, methods for their preparation were developed as indicated below.

The γ-form was prepared most conveniently at 25° by dropwise addition of methanol to a well-stirred aqueous solution containing 20% NH_4F and 0.5% UF_4. The precipitate was filtered and washed thoroughly with methanol. Larger crystals may be obtained by slow cooling of 15–20% NH_4F solutions initially saturated with U(IV) at 50°.

Typical procedures for preparation of the other forms follow:

(1) α-$(NH_4)_2UF_6$: A 22% NH_4F–0.6% UF_4 solution was diluted with three parts by weight of water and cooled in a brine bath to −3°. The resulting precipitate was filtered and washed with methanol at 0°.

(2) β-$(NH_4)_2UF_6$: A finely powdered sample of $(NH_4)_4UF_8$ was stirred with a 10% NH_4F solution for 15 min. at room temperature, filtered, and washed thoroughly with methanol.

(3) δ-$(NH_4)_2UF_6$: A finely powdered sample of the β-form was heated at 110° for 30 min.

Preparation of $7NH_4F \cdot 6UF_4$.—Addition of UF_4, $(NH_4)_2UF_6$, or $(NH_4)_4UF_8$ to dilute NH_4F solutions (less than about 1 *M*) yields $7NH_4F \cdot 6UF_4$ at room temperature, ordinarily after a few minutes of rapid stirring. The best crystallized sample of $7NH_4F \cdot 6UF_4$ was prepared by a 72-hr. digestion at 80° of the product obtained by addition of UF_4 to 8 *M* NH_4HF_2. (The *initial* product under these conditions was primarily γ-$(NH_4)_2UF_6$.)

The stoichiometry $7NH_4F \cdot 6UF_4$ was established by chemical analysis of products obtained both from NH_4HF_2 and NH_4F solutions. Separate experiments also confirmed that treatment of $(NH_4)_4UF_8$ with dilute NH_4F (0.5 to 1 *M*) removed 2.80 ± 0.03 moles of NH_4F per mole of U(IV) to give $7NH_4F \cdot 6UF_4$.

Interconversion among Forms of $(NH_4)_2UF_6$.—Proof of the constant stoichiometry of α-, β-, γ-, and δ-$(NH_4)_2UF_6$ was given by their interconversion without gain or loss of NH_4F. This was demonstrated by chemical analysis of each form and by analysis of alcohol extracts after conversion of other forms to the δ-form. Each of the other forms was converted rapidly to the δ-form in boiling ethanol but reconverted on cooling.

The dry powders of α-, β-, and γ-forms obtained from aqueous slurries by filtration and methanol washing usually remained in the same form indefinitely. However, preparation of dry powders of δ-form from hot (70°) aqueous slurries proved difficult since conversion to one of the other forms occurred during filtration. Samples of δ-form prepared by heating dry β-form (or by thermal decomposition of $(NH_4)_4UF_8$ at 92°) usually remained δ for several weeks but spontaneous conversion to the β-form was noted with several δ-form samples stored at room temperature.

A striking visual demonstration of interconversion of these forms is provided by the following cycle: A dry sample of slightly bluish green β-form held on filter paper in the vapors of boiling methanol changes immediately to the deep blue-green of the δ-form. Upon removal from the methanol vapors, immediate conversion to β-form is observed. The same sample warmed in dry air (held over a hot plate) changes again to δ-form, but now remains δ upon cooling to room temperature (>26°). If the sample is heated a second time in methanol vapors, it remains δ while hot but converts once again to β upon cooling to room tem-

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[12] We are indebted to Marvin C. Tinkle of this laboratory for supplying this material.

TABLE I

CRYSTALLOGRAPHIC PROPERTIES OF $(NH_4)_4UF_8$, γ-$(NH_4)_2UF_6$, AND $7NH_4F \cdot 6UF_4$

(1) $(NH_4)_4UF_8$
  (X-ray powder pattern ref. 8)
  Optical properties:
    Biaxial; positive
    $N_\alpha = 1.454$, $N_\gamma = 1.464$
    $2V \approx 90°$
    Pleochroic, pale brown-green to strong green
    Dispersion: strong, r > v
(2) γ-$(NH_4)_2UF_6$
  Optical properties:
    Biaxial; positive
    $N_x = 1.466$, $N_z = 1.493$
    $2V \approx 30°$
    Pleochroic: N_x = grass-green
      N_z = blue-green
    Optic orientation: $X = c$
      $Y = b$
      $Z = a$
    Dispersion: strong, r > v
  X-Ray diffraction data:
    Orthorhombic; $Pmc2_1$ or Pmcm
    $a_0 = 4.05$, $b_0 = 7.03$, $c_0 = 11.76$ Å.
    $Z = 2$
    ρ (X-ray) = 3.86, ρ (obsd.) = 3.9 g./cm.[3]
(3) $7NH_4F \cdot 6UF_4$
  Optical properties:
    Uniaxial; negative
    $N_0 = 1.518$, $N_\epsilon = 1.513$
    Color: light green, no dichroism
    Morphological habit: hexagonal dipyramids or small rhombohedrons
  X-Ray diffraction data:
    Hexagonal; $R\bar{3}$ or $P\bar{3}$ (powder diffraction data only; ref. 8)
    $a_0 = 15.40$, $c_0 = 10.49$ Å.
    (Rhombohedral; $a_0 = 9.55$ Å., $\alpha = 107.4°$)

TABLE II

PARTIAL X-RAY POWDER PATTERNS FOR α, β, AND δ POLYMORPHS OF $(NH_4)_2UF_6$

α		β		δ	
d, Å.	I	d, Å.	I	d, Å.	I
6.05	100	5.97	100	6.13	60
4.71	22	5.88	78	5.91	100
3.77	18	4.77	4	4.08	26
3.55	18	4.01	34	3.49	40
3.52	19	3.80	4	3.37	65
3.21	58	3.48	24	3.06	7
3.16	21	3.44	20	2.96	13
3.04	16	3.42	22	2.65	17
2.825	8	3.37	24	2.60	8
2.795	8	3.33	57	2.45	9
2.578	5	3.23	8	2.39	20
2.566	10	3.19	4	2.27	13
2.370	19	3.02	10	2.22	7
2.315	9	2.99	10	2.04	10
2.300	11	2.94	10	2.01	13
2.199	15	2.65	8	1.98	17
2.190	22	2.63	11	1.93	17
2.049	10	2.59	13		
2.037	9	2.42	11		
1.973	16	2.39	17		
1.963	16	2.36	13		
1.942	14	2.28	11		
1.893	6	2.23	10		

CALCULATED AND OBSERVED d-SPACINGS FOR γ-$(NH_4)_2UF_6$[a]

hkl	d_{calcd}, Å.	d_{obsd}, Å.	I_{obsd}
011	6.03	5.99	100
002	5.88	5.81	51
100	4.05	4.03	25
020	3.51	3.51	17
013	3.42	3.40	24
111	3.36	3.34	47
102	3.33	3.32	25
022	3.02	3.00	12
004	2.94	2.91	6
120	2.65	2.65	8
113	2.61	2.60	12
122	2.41	2.41	16
104	2.38	2.37	11
031	2.30	2.29	8
024	2.25	2.24	5
015	2.23	2.21	7
200	2.02	2.01	7
033	2.010	1.994	12
131	1.998		
124	1.970	1.961	10
006	1.960	1.943	11
115	1.954		
211	1.918	1.912	12
202	1.914		

[a] Identification of closely spaced lines was aided by intensity of reflections in precession photographs.

perature. Similar (though somewhat more subtle) color changes are observed when the β- or γ-forms are converted to the green α-form on cooling in vapors of liquid nitrogen.

Spectra of $(NH_4)_2UF_6$.—The spectra of α-, β-, γ-, and δ-$(NH_4)_2UF_6$ are shown in Fig. 1. The differences in the visible spectra provided the principal clue to the existence of these several types of $(NH_4)_2UF_6$ and proved convenient for rapid identification throughout the preparative work. The spectra were obtained using mulls with petrolatum or silicone grease. Spectra were also obtained of the finely divided material in contact with the mother liquor using slurries contained in polyethylene bags.

Crystallographic Properties.—Optical and X-ray crystallographic properties are presented in Table I.

The diffraction patterns of the four $(NH_4)_2UF_6$ polymorphs were recorded with a Norelco X-ray spectrometer for graphic display of their differences; the patterns are presented in Fig. 2. Table II lists the d-spacings and relative intensities of the α-, β-, and δ-$(NH_4)_2UF_6$ polymorphs and the indexed pattern of γ-$(NH_4)_2UF_6$. γ-$(NH_4)_2UF_6$ is the form in equilibrium at 25° with NH_4F solution and was the only polymorph yielding single crystals large enough for X-ray or optical study.

There is no evidence for polymorphism in the case of crystalline $(NH_4)_4UF_8$, but the structure is complex and has not been analyzed in detail. Crystals of $(NH_4)_4UF_8$ are almost always twinned and readily lose NH_4F to the atmosphere. Diffraction patterns from $(NH_4)_4UF_8$ show strong pseudohexagonal symmetry with angles of 118° ± 30′ but the crystals are optically biaxial, precluding true hexagonal symmetry.

The X-ray powder patterns for $(NH_4)_4UF_8$ and $7NH_4F \cdot 6UF_4$ were reported earlier[8]; the anhydrous preparations yielded only fine powders whose optical properties could not be measured.

Spectra of U(IV) in NH_4F Solutions.—In aqueous NH_4F solution, U(IV) shows regions of strong absorption around 1100 and 650 mμ. The detailed form and absorbancy of these peaks varies markedly with NH F concentration as shown in Fig. 3.

The spectra were also found to change slightly with U(IV) concentration at moderately high but constant NH_4F concentration despite the fact that the accessible U(IV) concentration range is very limited (0–0.02 M). In particular, the molar extinction coefficient at the maximum of the sharp peak at 662 mμ decreases as shown in Fig. 4 with increasing U(IV) concentration in 7 M NH_4F but remains constant in 12 M NH_4F. The line in Fig. 4b

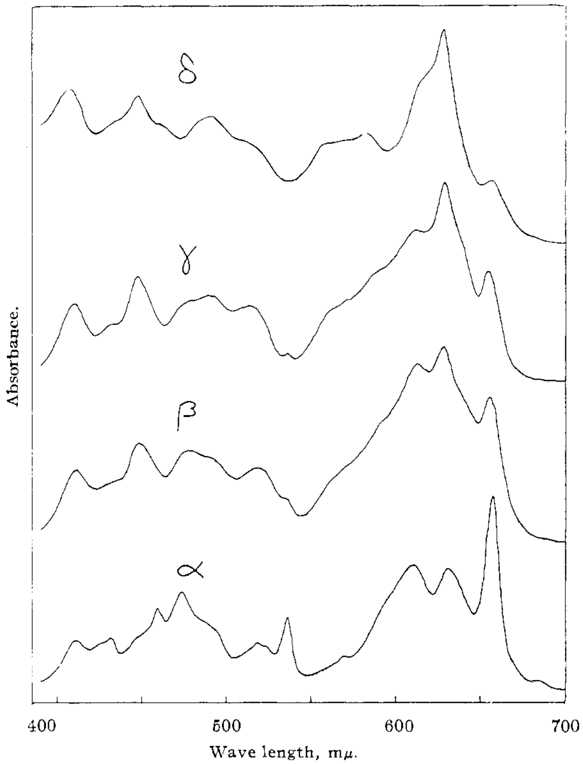

Fig. 1.—Absorption spectra of mulls of α-, β-, γ-, and δ-$(NH_4)_2UF_6$.

is given by $E = 29.4 - 200M$ where M is the U(IV) molarity. In contrast, the molar extinction coefficient of the broader peak at 615 mμ is independent of U(IV) concentration throughout the range from 7 M to saturated NH_4F so that measurements at this wave length are suitable for quantitative determination of U(IV) concentrations. As was indicated in Fig. 3, however, the molar extinction coefficient at 615 mμ varies with the NH_4F concentration, so that a calibration curve must be constructed as described in the next section.

Spectrophotometric Determination of U(IV) in NH_4F Solution.—The molar extinction coefficients of U(IV) were determined at 615 mμ in 7 M to saturated NH_4F. The observed values increased monotonically from 21.1 to 25.6 M^{-1} cm.$^{-1}$. The solutions used for these measurements were prepared by weight in Teflon bottles and rotated for several days to ensure complete dissolution of the UF_4. Tin shot was added to prevent oxidation of U(IV) by trace amounts of oxygen. The measurements of optical density were obtained using a constant temperature cell compartment maintained at 25°. The precision of the absorbance measurements was 0.5%. About 20 independent measurements of the extinction coefficients showed a scatter of about 1.5% around a smooth curve.

The $(NH_4)_2UF_6$–$(NH_4)_4UF_8$ and $(NH_4)_4UF_8$–NH_4F Univariant Points at 25°.—Samples for determination of these invariant points in the NH_4F–UF_4–H_2O system were prepared in triplicate by weight in Teflon bottles and rotated for at least 5 days in a water bath held at 25°. If the U(IV) was added as $(NH_4)_4UF_8$ (prepared separately) equilibration appeared complete after 2 days. The U(IV) concentration in solution was determined spectrophotometrically. The NH_4F concentration was determined by replacement of the ammonium ions by hydrogen ions using standard ion-exchange techniques and titration of the resulting HF solution to the phenolphthalein end point. Correction for the contribution of U(IV) present in the saturated solutions was made with the assumption that each U(IV) ion displaced four H^+ ions from the resin. Identification of the solids in the equilibrium mixtures was made by optical examination using the petrographic microscope.

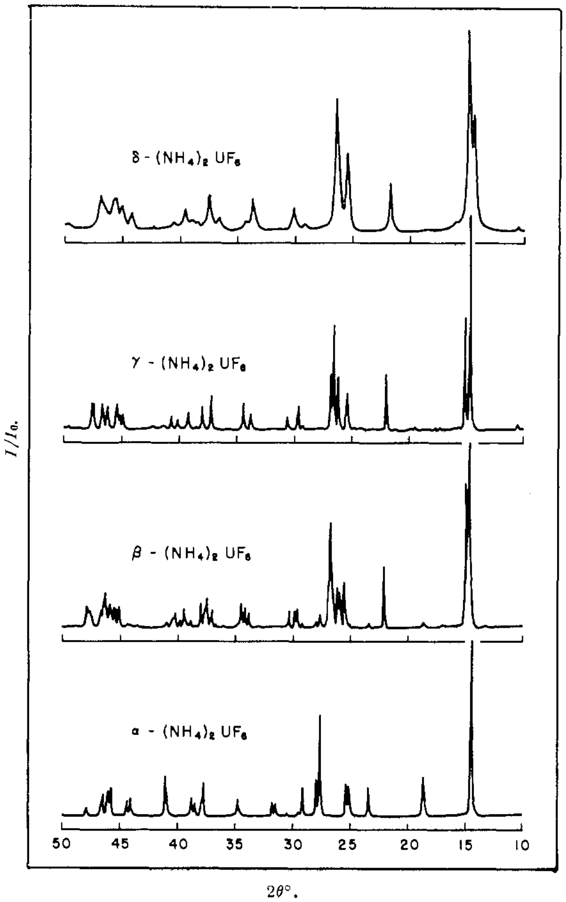

Fig. 2.—X-Ray spectrometer tracings of α-, β-, γ-, and δ-$(NH_4)_2UF_6$ (Cu Kα radiation).

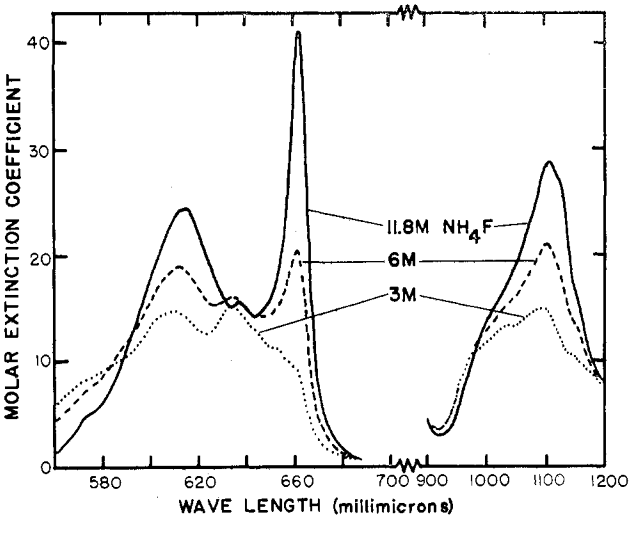

Fig. 3.—Absorption spectra of U(IV) in concentrated NH_4F solutions. The U(IV) concentrations used were 0.01, 0.005, and 0.0025 M at 11.8, 6, and 3 M NH_4F, respectively.

In the three experiments at the $(NH_4)_2UF_6$–$(NH_4)_4UF_8$ isothermal invariant point, the quantities of reagents were chosen so that the two solid phases were present at equilibrium in mole ratios of approximately 3:1, 1:1, and 1:3. No indication of a third phase such as $(NH_4)_3UF_7$ was obtained. Identification of the $(NH_4)_2UF_6$ as the γ-form depended on separate equilibrations at 25° in which the NH_4F concentration was held slightly below the invariant point concentration.

Results of these experiments are presented in Table III.

TABLE III

UNIVARIANT POINTS IN THE NH_4F–UF_4–H_2O SYSTEM AT 25°

	NH_4F		UF_4	
Solid phases	Wt. %	Molality	Wt. %	Molality
$(NH_4)_4UF_8$–NH_4F	45.1	22.3	0.378	0.0222
$(NH_4)_2UF_6$–$(NH_4)_4UF_8$	24.2	8.71	0.632	0.0268

Equilibria Involving $7NH_4F \cdot 6UF_4$.—Attempts to determine the $7NH_4F \cdot 6UF_4$–$(NH_4)_2UF_6$ isothermal invariant point were abandoned when it was found that equilibria involving the 7:6 compound were reached extremely slowly. Even though $(NH_4)_2UF_6$ is converted to $7NH_4F \cdot 6UF_4$ immediately upon treatment with dilute NH_4F, the reverse of this reaction could never be observed. Indeed, $7NH_4F \cdot 6UF_4$ was left as an insoluble residue when its mixtures with $(NH_4)_2UF_6$ were leached repeatedly with 6 *M* NH_4F. Further, a sample of $7NH_4F \cdot 6UF_4$ stirred in 7 *M* NH_4F for 40 days at 25° remained unchanged and did not convert to $(NH_4)_2UF_6$ as expected even though the composition was chosen very close to the $(NH_4)_2UF_6$–$(NH_4)_4UF_8$ isothermal invariant point.

Solubility of $(NH_4)_4UF_8$ at 25°.—As in the experiments described in previous sections, samples were prepared by weight in Teflon bottles and equilibrated at least 5 days at 25°. The U(IV) concentrations at equilibrium were determined spectrophotometrically. The results are shown in Fig. 5.

Anion-Exchange Absorption of UF_4.—No absorption of U(IV) by anion-exchange resin (Dowex 1X8) in the fluoride form was observed visually from NH_4F solutions more concentrated than about 0.5 *M*. However, rotation of a slurry of fluoride-form resin and UF_4 in *water* resulted in absorption of the UF_4 within 4 to 48 hr. The maximum amount absorbable under these conditions was determined by observing a series of samples with various weight ratios of UF_4 to resin. Even very small amounts of residual UF_4 (or, more precisely, $UF_4 \cdot 2.5H_2O$) could be observed by microscopic examination of the slurry. Complete absorption was observed within 2 days with 0.60 mole of UF_4 per equivalent of exchange capacity. Absorption was incomplete with 0.62 (or more) mole of UF_4 per equivalent of resin even after 20 days equilibration.

Spectra of U(IV) in the saturated (dark green) resin showed absorption maxima (in order of decreasing intensity) at 629, 1047, 1080, 600, and 427 mμ. The spectra were obtained using a special cell of 2-mm. path length. The observed peak positions and relative intensities were shifted from any observed in the complex salts but were similar to those in dilute NH_4F solutions.

Discussion

Properties of the Solids.—Since crystalline $(NH_4)_4UF_8$ exists in equilibrium with saturated aqueous solution and excess solid NH_4F, it is the complex with the highest $NH_4F:UF_4$ ratio in the NH_4F–UF_4–H_2O system at 25°. It is stable in contact with a wide range of aqueous NH_4F concentrations, from 24.2 to 45.1 wt. % (7.07 to 13.6 *M*). This compound type is formed typically by actinide tetrafluorides in contact with concentrated NH_4F solutions, yielding the isostructural series: $(NH_4)_4UF_8$ (green); $(NH_4)_4NpF_8$ (yellow-green)[6]; $(NH_4)_4PuF_8$ (pink)[7]; and $(NH_4)_4AmF_8$ (red).[3] Compounds of analogous composition are $4HF \cdot UF_4$[13] and $Rb_4U(SCN)_8$.[14]

In fused melts between UF_4 and the alkali fluorides, this $4MF \cdot UF_4$ type is formed only between LiF and UF_4.[15] With the rest of the alkali fluorides and UF_4 the 3:1 type is common.[16] It is worthy of note that $(NH_4)_3UF_7$ was not found in work on the thermal decomposition[8] of $(NH_4)_4UF_8$ nor was it found in the present work, although the rubidium compound of 3:1 stoichiometry, Rb_3UF_7, is well known.[9] Furthermore, $(NH_4)_2UF_6$ and Rb_2UF_6 are not isostructural.[17] Since the ionic size and charge of NH_4^+ and Rb^+ are essentially the same, other factors must play a role in determining both stoichiometry and crystal structure of these complexes.

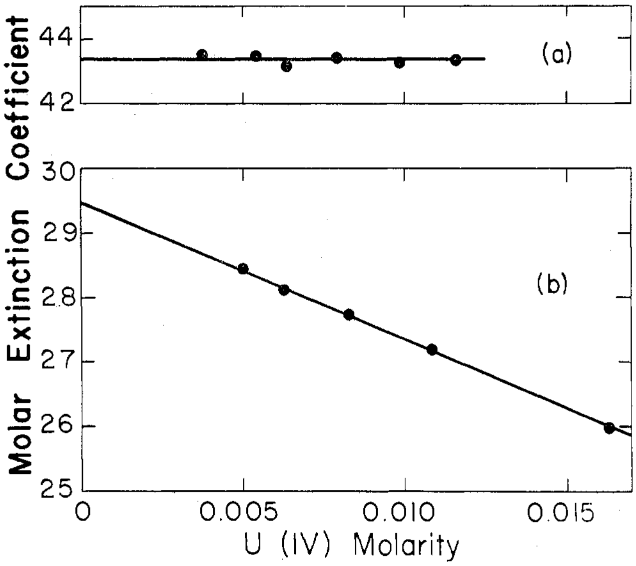

Fig. 4.—Molar extinction coefficient of U(IV) at 662 mμ as a function of U(IV) molarity: (a) 7 *M* NH_4F solution; (b) 12 *M* NH_4F solution.

Compounds having the stoichiometry $(NH_4)_2UF_6$ were found to give four types of absorption spectra and, correspondingly, four X-ray powder patterns (see Fig. 1 and 2). Transitions from the highest temperature form to the lowest temperature form occurred within about 75°. This remarkably narrow temperature range indicates that the lattice energy differences among these four forms are very small. The structural differences which give rise to four forms of $(NH_4)_2UF_6$ may involve fluoride bridging and hydrogen bonding in varying degrees. Hydrogen bonding in this case should not be strong and would partake in structural configurations which could be altered by relatively small temperature changes. These same interactions must be responsible for the twinning of $(NH_4)_4UF_8$, the reported polymorphs of NH_4UF_5,[8] and the structural relation of $7NH_4F \cdot 6UF_4$ and α-NH_4UF_5. Detailed single crystal structure analyses are being carried out on $(NH_4)_4UF_8$ and γ-$(NH_4)_2UF_6$. The occurrence of polymorphism also has been reported for U(IV) fluoride complexes formed with alkali fluorides[18] such as α-, β_1-, and β_2-K_2UF_6, α-, β_2-, and γ-Na_2UF_6, and α- and β_1-K_2ThF_6, wherein hydrogen bonding could not be in-

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(13) I. V. Tananaev and G. S. Savchenko, *Atomnaya Energ.*, **12**, 397 (1962); *Chem. Abstr.*, **58**, 1110 (1963).

(14) V. P. Markov and E. N. Traggeim, *Zh. Neorgan. Khim.*, **6**, 2316 (1961); *Chem. Abstr.*, **58**, 11172 (1963).

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(18) W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948).

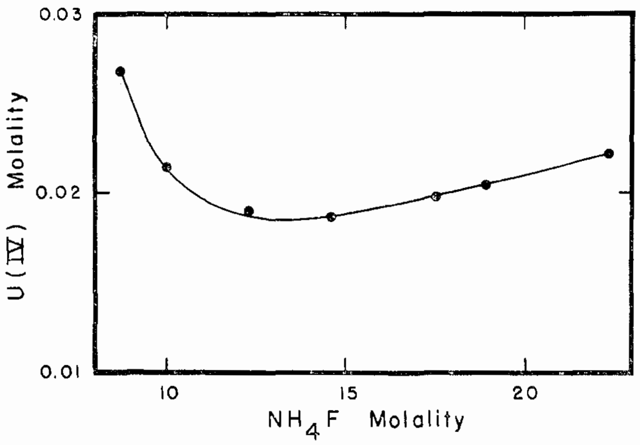

Fig. 5.—Solubility of $(NH_4)_4UF_8$ in NH_4F solutions. The solid curve is given by $[U(IV)] = 655[NH_4F]^{-5} + 0.00465[NH_4F]^{1/2}$.

volved. Gruen[19] has reported the spectra of δ-Na_2UF_6. Its room temperature spectrum bears a strong resemblance to the spectrum of δ-$(NH_4)_2UF_6$ shown in Fig. 1.

In the previous work involving the anhydrous system NH_4F–UF_4, the compound $7NH_4F{\cdot}6UF_4$ was prepared as a fine powder.[8] In the present solution work we were able to obtain small single crystals. Optical measurements confirmed the reported hexagonal symmetry.[8] The occurrence of 7:6 compounds in other fluoride systems has been explained on the basis that there is space for an extra molecule of MF per 6 molecules of $MF{\cdot}UF_4$ in the crystal lattice.[20] In the section entitled "Equilibria Involving $7NH_4F{\cdot}6UF_4$," it was shown that this phase is formed readily from solution, but once formed it is very slow to dissolve in or add NH_4F from NH_4F solutions.

Solubility of $(NH_4)_4UF_8$.—The solubility of $(NH_4)_4UF_8$ and, hence, the chemical potential of the solution component $(NH_4)_4UF_8$ varies rather little with NH_4F concentration with only about a 35% change in solubility over its entire range of stability. The highest solubility at 25° was observed at the $(NH_4)_2UF_6$–$(NH_4)_4UF_8$ isothermal invariant point at which the U(IV) and NH_4F molalities were 0.0268 and 8.71, respectively. The solubility decreases with increasing NH_4F concentration to a shallow minimum near 0.0185 molal U(IV) and 14 molal NH_4F, then increases slowly to the $(NH_4)_4UF_8$–NH_4F invariant point.

The solubility may be represented in terms of molalities by

$$[U(IV)] = 655[NH_4F]^{-5} + 0.00465[NH_4F]^{1/2} \quad (1)$$

The initial decrease in solubility may be attributed to the common ion effect and, in particular, the first term on the right-hand side of eq. 1 may be identified formally with the equilibrium

$$UF_7^{-3} + F^- + 4NH_4^+ \rightleftarrows (NH_4)_4UF_8\ (solid)$$

The increase in solubility toward the highest NH_4F concentrations is found empirically to be proportional to $[NH_4F]^{1/2}$. The major part of this increase is likely due to "salting in" of the U(IV)-containing species (*i.e.*, to a decrease in their activity coefficients). However, formation of one or more higher complex species (*e.g.*, UF_8^{-4}) might well contribute to the observed slope. The spectrophotometric observations discussed in the next section give an indication of interaction between U(IV) ions at the lower NH_4F concentrations studied. Such interaction may contribute to the observed trends in solubility and, in particular, dimerization occurring with evolution of F^- ions would tend to contribute to the initial decrease.

These conclusions, although necessarily very qualitative, appear consistent with the results of Savage and Browne[11] on the solubility of UF_4 in dilute HF. They suggest that the anionic species UF_5^- and UF_6^{-2} become important at F^- concentrations above about 0.01 molal and report an equilibrium constant for the reaction $UF_5^- + F^- \leftrightarrows UF_6^{-2}$ of 200 at an ionic strength of 0.12. At the very high F^- concentrations used in the present study, formation of UF_6^{-2} would be complete and formation of higher complexes would be strongly favored.

Spectra of U(IV) in Concentrated NH_4F Solution.—In studying the solution spectra of U(IV), our attention has been centered on possible information regarding the nature of the solution species. Visible spectra have proved useful for indicating the principal species in solution.[21] Changes in the detailed form of the U(IV) spectra may be expected to reflect changes in the number or arrangement of F^- ions around each U(IV).

Three principal trends with increasing NH_4F concentration may be discerned in the solution spectra of U(IV) in the region around 650 mμ (see Fig. 3): (1) the fairly broad peak around 615 mμ shifts toward longer wave lengths; (2) the peak around 630 mμ becomes less and less prominent; (3) the absorption at 662 mμ increases continuously.

These observations imply that throughout the range of NH_4F concentrations studied (2–13 *M*) changes occur in the nature of the immediate environment of the U(IV) ions, or, in other words, in the nature of the U(IV)-containing species. Such changes are most naturally ascribed to an increase with NH_4F concentration in the average number of F^- coordinated with each U(IV). Certainly this evidence weighs against the persistence of a single well-defined species such as UF_6^{-2} in the sense that NbF_6^- apparently persists in aqueous HF solutions.[22]

In contrast with Nb(V), the U^{+4}:F^- radius ratio (0.684) permits formation of a stable eightfold coordination polyhedron. The spectrum of U(IV) in >10 *M* NH_4F has a striking resemblance to the spectrum of the solid $(NH_4)_4UF_8$. Further, the spectrum of anion exchanger saturated with UF_4 (in which the U(IV) evidently is coordinated on the average with

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[19] D. M. Gruen, *J. Am. Chem. Soc.*, **76**, 3850 (1954); for detailed analyses of U(IV) spectra see: J. G. Conway, *J. Chem. Phys.*, **31**, 1002 (1959); R. A. Satten, D. J. Young, and D. M. Gruen, *ibid.*, **33**, 1140 (1960); S. A. Pollack and R. A. Satten, *ibid.*, **36**, 804 (1962).

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[22] O. L. Keller, Jr., *Inorg. Chem.*, **2**, 783 (1963).

between five and six F^-) is similar to spectra obtained at the lowest NH_4F concentrations (2 M) which could be studied. These observations are consistent with the hypothesis that the average ligand number is about six in 2 M NH_4F and approaches eight in saturated NH_4F.

As noted in the Experimental section, the molar extinction coefficient of U(IV) at 662 mμ, E_{662}, shows a fairly small but clearly established decrease with increasing U(IV) concentration in 7 M NH_4F (see Fig. 4). In contrast, E_{662} is independent of U(IV) concentration in 12 M NH_4F. These observations can be explained assuming that U(IV) forms dimers (or other polymers) with a low E_{662} in 7 M NH_4F and that these are depolymerized in the presence of very high F^- concentrations. Such dimers might well involve hydroxide or oxide bridging, particularly since the NH_4F solutions are slightly basic. However, at least one case of fluoride bridging is well established,[23] and this may constitute another example. The observed decrease ($E_{662} = 29.4 - 200M$) is consistent with the formation of dimers with a constant $K_d = [\mathrm{U(IV)}_2]/[\mathrm{U(IV)}]^2$ greater than 3.4 l./mole. This minimum value is obtained if E_{662} for the dimer is assumed equal to 0.

Anion-Exchange Absorption of UF_4.—Dissolution of insoluble salts by cation exchangers is well known (*e.g.*, $BaCO_3$ by H^+-form resin).[24] The absorption of UF_4 by fluoride-form anion exchanger differs in that no reaction product is given off, but instead the UF_4 enters the resin and adds to the exchangeable F^- originally present. The anion-exchange absorption of UF_4 from a water slurry provides a striking demonstration of the tendency of U(IV) to form anionic complexes with F^-. Examination of the U(IV) spectrum also is made possible in a system similar in many respects to aqueous solutions but with the additional advantage that an indication of the ligand number may be obtained from the stoichiometry. This type of ion-exchange absorption has apparently not been reported previously. It should be useful with a wide variety of systems in which complex anionic species are formed readily.

In the Experimental section it was noted that saturation was reached when 0.60 mole of UF_4 were absorbed for each mole of F^- originally present in the resin. Thus, for each 0.6 mole of U(IV) there are 3.4 moles of F^-. This composition is consistent with the presence of 0.4 mole of UF_6^{-2} and 0.2 mole of UF_5^- per equivalent of exchange capacity. This high degree of absorption of $UF_4 \cdot 2.5H_2O$ (which is very sparingly soluble in water) indicates correspondingly large formation constants for UF_5^- and UF_6^{-2} in the resin phase. In fact, the absorption can be most readily explained by assuming a formation constant $k = (UF_5^-)/(UF_4)(F^-)$ several orders of magnitude larger than that found in dilute HF solutions.[11] On the other hand, the visible spectra of resin samples containing only small amounts of UF_4 were indistinguishable in form from those of resin saturated with UF_4. This suggests that higher complexes such as UF_7^{-3} and UF_8^{-4} have far less tendency to form within the resin than in concentrated NH_4F solutions.

Acknowledgment.—It is a pleasure to acknowledge the technical assistance of Mr. Edward Bosier and Miss Suzanne Krainock.

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The Formation of a Neptunium(V)-Chromium(III) Complex. Kinetics and Equilibria in Perchlorate Solutions[1]

BY JAMES C. SULLIVAN

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A value for the equilibrium quotient $Q = [\mathrm{Np(V)\cdot Cr(III)}]/[\mathrm{Np(V)}][\mathrm{Cr(III)}]$ of 2.62 ± 0.48 at 25° has been determined spectrophotometrically. Values of $\Delta H = -3.3 \pm 0.6$ kcal. and $\Delta S = -9.0 \pm 1.9$ e.u. have been determined. The rates of formation and aquation of the complex Np(V)·Cr(III) have been measured. The complex is also formed by the reduction of Np(VI) with Cr(II).

Introduction

It has been demonstrated previously that Np(V) and Cr(III) ions, in aqueous perchloric acid-perchlorate media, react to produce a substituted chromic complex ion.[2] A detailed study of the thermodynamic and kinetic variables of this reaction is of interest since (a) complex ion formation between cations, in a noncomplexing medium, extends our knowledge of ionic interactions in solution; (b) this represents a convenient system to study the properties of a species analogous to the intermediates U(V)-Cr(III)[3] and Pu(V)-Fe(III)[4] which have been investigated by Newton in the course of kinetic studies.

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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