solution containing an excess of chloride ion, so that when crystallization is complete the supernatant liquid should have only a faint green coloration. The yield of $Nb_6Cl_{14}\cdot 7H_2O$ from 28 g. of $NbCl_5$ was usually about 6.5 g. (32%).

The procedure described above was used for the preparation of 45 g. of $Nb_6Cl_{14}\cdot 7H_2O$. This quantity was obtained as the combined products of eight successive runs in which the yields, calculated on the basis of the amount of $NbCl_5$ used, ranged from 29 to 44%.

Acknowledgment.—We wish to express our indebtedness to Professor Linus Pauling for his stimulating interest in this investigation.

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY, LOS ALAMOS, NEW MEXICO]

The Solubility of Uranium (IV) Fluoride in Aqueous Fluoride Solutions[1,2]

BY ALBERT W. SAVAGE, JR., AND JAMES C. BROWNE

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The solubility of $2UF_4\cdot 5H_2O$ was measured at 25.0° as a function of fluoride ion concentration in mixtures of hydrofluoric and perchloric acids at a constant ionic strength of 0.12 m. Uranium was determined by radioassay using U^{233} as a tracer. Equilibrium was established by approaching from both sides. The behavior of the equilibrium solubility, which varied from $1.35 \times 10^{-3}\ m$ at $[F^-] = 1.9 \times 10^{-5}\ m$, through a minimum of $0.12 \times 10^{-3}\ m$ at $[F^-] = 9.6 \times 10^{-4}\ m$, to 0.37×10^{-3} m at $[F^-] = 1.5 \times 10^{-2}\ m$, is best explained by the existence in solution of the species UF_2^{++}, UF_3^+, UF_4^0 UF_5^-, and $UF_6^=$.

Introduction

There does not appear to have been any extensive investigation, prior to the present study, of the solubility of UF_4 as a function of fluoride ion concentration. According to Katz and Rabinowitch[3] the most reliable value for the solubility of UF_4 in water at 25° is 10^{-4} mole per liter as determined by R. Kunin. This value is in good agreement with that previously found by investigators[4] who reported the molality of a saturated solution of uranium tetrafluoride in oxygen-free water at 25.0° to be $(1.03 \pm 0.03) \times 10^{-4}$, and at 40.2° to be $(1.94 \pm 0.03) \times 10^{-4}$. They reported equilibration for at least 300 hr. in glass apparatus under a nitrogen atmosphere.

The present investigation was carried out in acid solution to avoid hydrolysis complications[5] and the use of glass apparatus was avoided. A comprehensive effort was made to insure equilibrium conditions by approaching from both sides by an imposed temperature variation.

Experimental

Apparatus and Materials.—All solutions were equilibrated in a platinum cup $2^3/_8''$ in diameter and 4" high. This cup fitted loosely in a Pyrex jacket equipped with a standard taper 71/60 male joint. The Pyrex cover contained three tubes. The two outer ones were vents for flushing with hydrogen and were equipped with stopcocks. The central tube extended down to a level $1^1/_2''$ above the top of the platinum cup and ended in a standard taper female joint. Into this was fitted a tapered platinum male joint connected to a $^1/_8''$ i.d. platinum tube which extended down to within $^3/_4''$ of the bottom of the cup, flaring out at the end into a sintered platinum frit one inch in diameter. Through this tube samples could be filtered at the temperature of the solution and withdrawn for analysis. All joints and stopcocks were greased with Apiezon "N" lubricant. Fig. 1 shows this assembly.

The cup and container rested on a water-tight Lucite box which was built to house a "Mag-mix" motor, and the whole assembly was immersed in a 27" × 27" × 24" water bath. The bath temperature was measured with a platinum resistance thermometer and was controlled to better than ± 0.01°. The solutions were stirred magnetically by means of a platinum-covered iron magnetic rod $1^1/_2''$ long and $^1/_2''$ in diameter. Because of wear from the platinum-platinum contact with the cup, stirring was done only intermittently.

Samples were withdrawn into commercial weight burets fitted with side arms and stopcocks so that a vacuum could be applied. For runs involving higher concentrations of HF, burets constructed of Lucite were substituted, and the glass parts of the solubility apparatus were coated with melted paraffin.

The solvents were prepared from reagent grade 60% perchloric acid, 48% hydrofluoric acid and redistilled water. The perchloric acid solutions were titrated with sodium carbonate as a primary standard, using a methyl orange xylene cyanole indicator. The hydrofluoric acid was poured into a Lucite weight buret and diluted with water if necessary; weighed portions were titrated with standard NaOH solutions according to the method given.[6] At no time was any fluoride solution allowed to come into contact with any silica. The two acids were mixed in the desired proportions by weight in a polythene bottle.

The solid phase was determined to be $2UF_4\cdot 5H_2O$ by analysis and confirmed by microscopic examination of its optical properties. Two separate portions were prepared, by two different methods, and both products exhibited essentially the same solubility. In the first case uranium peroxide was precipitated from a uranyl nitrate solution containing about 1.4% of the uranium as U^{233}. The peroxide was ignited in air at 850° for 14 hr., converting it to U_3O_8. Since the saturated UF_4 solutions were to be analyzed for total uranium by counting the radioactivity, a portion of this tagged U_3O_8 was reserved for use as a primary standard in determining the specific count rate. The balance was converted to anhydrous UF_4, first by reduction with hydrogen gas to UO_2 at 700°, and then by hydrofluorination with anhydrous HF and H_2 gases at 550° for 5 hr. and then 4 hr. of sintering at 825° in a platinum boat. Approximately 10 g. of tagged UF_4 was so produced, and most of this material was consumed in the preliminary experiments involved in establishing the experimental procedures which finally were adopted.

In the second case uranium peroxide was precipitated from a uranyl solution containing 2.24 g. of U^{233} and 45 g. of U^{238}. About 3 g. of the peroxide was ignited to constant weight at 850°. The remainder of the peroxide was dissolved in dilute aqueous HF in a polythene beaker. The solution was electrolyzed using platinum electrodes

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] A preliminary account was presented before the 135th National Meeting of the American Chemical Society, Boston, April 6, 1959.

[3] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," National Nuclear Energy Series, Div. VIII, Vol. V, McGraw-Hill Book Co., New York, N. Y., 1951, p. 372.

[4] H. A. Bernhardt, J. H. Junkins and S. S. Kirslis, *AECD-3412*, June 15, 1949 (declassified).

[5] *Cf.* K. A. Kraus and F. Nelson, THIS JOURNAL, **72**, 3901 (1950).

[6] "Reagent Chemicals, A.C.S. Specifications," 1950, p. 172.

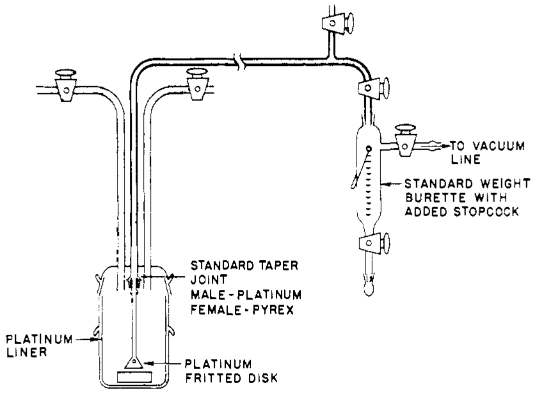

Fig. 1.—Solubility apparatus.

and an applied voltage of 2.3 volts. The resulting green precipitate was washed by decantation.

In each case the product was digested several days with 2 to 3% hydrofluoric acid at room temperature, converting the material into light green acicular crystals of $2UF_4 \cdot 5H_2O$.

Procedure.—A few grams of the solid phase was placed in the platinum cup. This material was washed and vacuum dried before each run. The solid then was washed with several small portions of the solvent to be used and finally covered with about 200 g. of solvent. The apparatus was then assembled and immersed in the water-bath.

It was observed that acidic uranous solutions of approximately millimolar concentration in uranium oxidize to the hexavalent (uranyl) state almost completely after a few hours exposure to air. It also was found that the passage of hydrogen gas for 1 hr. through an acidified millimolar uranyl fluoride solution in a glass container had no appreciable effect on the oxidation state of the uranium, but when a small coiled strip of platinum metal was placed in the solution in such a position that the bubbles of hydrogen came in contact with the platinum, polarographic tests showed the uranium to be over 99% reduced to the tetravalent state within an hour. Therefore in all solubility runs hydrogen gas was forced through the platinum frit and allowed to bubble through the solution for at least 1 hr. The hydrogen was passed first through a solution of approximately the same HF concentration as that in the solvent being used, to reduce the possibility of changing the HF concentration in the solution.

Equilibration at 25.0° under the hydrogen atmosphere was allowed to proceed until successive samples taken at least one day apart showed no appreciable difference in uranium concentration. Normally less than two days were required to reach equilibrium. The temperature was then raised to 35°, a sample was removed and the temperature was brought back to 25.0°. Samples were removed as before and compared with those taken before raising the temperature.

The samples collected in the weight burets were analyzed for total uranium by depositing weighed quantities on two-inch platinum disks, drying under an infrared lamp, heating in an oven at 500° for 45 minutes and then counting the alpha activity, using a proportional internal sample chamber with a methane flow and a Los Alamos PA-6 pulse amplifier and SC-3B scaler. The deposit consisted of from 20 to 60 individual droplets distributed over each plate to reduce masking of counts by heavy local concentrations of residues which tend to form around the edges of larger puddles on evaporation. It was found that heating at 500 to 550° produced the maximum count rate and that heating above 550° or for longer than 45 minutes never increased this rate and occasionally reduced it, probably through loss of material. After the first counting the plates were reheated at 550° and counted again. All checks included at least 1,000,000 counts so as to reduce the standard deviation resulting from statistical fluctuations in the count rate to 0.1%.

The specific count rate, in terms of counts per minute per microgram of the tagged uranium as registered under the conditions encountered in the actual measurements of the UF_4 residues, was determined by taking the ignited U_3O_8 as a primary standard. Weighed portions were dissolved in nitric acid, and the solutions were diluted to known weights in weight burets. Samples then were weighed out onto the platinum disks. The droplets were evaporated to remove excess acid, the residues were redissolved in droplets of water and treated with dilute hydrogen peroxide. It was found that more consistent results were obtained with the peroxide residues than with the plain uranyl nitrate. The plates, after drying, were heated at 500°, counted, reheated at 550° and counted again as a check. Values of 143 and 546 counts per minute per microgram of uranium were obtained respectively for the two different batches of tagged uranium prepared. In these calculations corrections for the isotopic weight of U^{233} were applied to the atomic weight of the uranium.

Results

The observed relationship between the concentration of added hydrofluoric acid and the resulting concentration of the total dissolved uranium in the saturated solutions at 25.0° is given in Table I.

TABLE I

VARIATION OF URANIUM CONCENTRATION WITH SOLVENT COMPOSITION

α Represents the total uranium concentration at equilibrium at 25.0° as calculated from the observed alpha activity. The composition of the solvent is given by β, the stoichiometric concentration of hydrofluoric acid and the concentration of perchloric acid as δ; all concentrations being expressed in moles per 1000 g. of solution.

Run	Obsd. [U] ($\alpha \times 10^3$)	HF (β)	$HClO_4$ (δ)
1	1.20	0	0.1009
2	1.37	0	.1212
3	1.35	0	.1212
4	0.72	0.00235_3	.1211
7	.39	$.00512_2$	.1212
8	.221	$.00996_5$	.1212
6	.120	.1117	.1199
10	.152	.597	.1047
11	.196	.981	.0843
5	.220	1.148	.0646
9	.37	1.98	0

Run number 1 was made with the first portion of tagged UF_4; all subsequent runs were made with the UF_4 prepared from the electrolytic reduction of the uranyl fluoride.

Table II shows the results for run 8, a typical case in the low-fluoride region.

In each pair of values for a given plate the higher value was taken as the more reliable, since either the masking due to incomplete removal of the insufficiently heated material, or the volatilization of uranium compounds due to excessive heating or any other loss of uranium, would tend to lower the count rate. The value 0.221×10^{-3} mole of uranium per 1000 g. of solution was taken as the most probable equilibrium value.

In the runs made in solutions of higher fluoride concentration, the return to equilibrium at 25 from 35° was not as precise and in fact went slightly below the value observed in the first samples and continued to decrease. The effect was interpreted as due to a loss of HF from the solution. Neither coating the exposed glass portions of the outer case of the apparatus with paraffin nor increasing the concentration of the HF in the hydrogen gas wash bottle seemed to have much effect. The hydrogen sweep was held to what was felt to be the mini-

TABLE II

VARIATION OF COUNTING DATA

Sample	Equilib. T, °C.	Days at temp.	Plate	T, °C.,[a] heating	c./m./mg.[b]	U[c]
1	25.0	2	1	500	28.63	0.221
				550	28.57	
			2	500	29.11	.224
				550	29.06	
			3	500	28.69	.221
				550	28.63	
2	25.0	6	1	500	28.70	.221
				550	28.67	
3	35	1	1	500	48.27	
				550	48.90	.377
			2	500	48.34	
				550	48.39	.373
4	25.0	1$^1/_2$	1	500	28.19	.217
				550	27.83	
			2	500	28.92	.223
				550	28.78	
			3	500	28.66	.221
				550	28.63	
5	25.0	4$^1/_2$	1	500	28.65	
				550	28.68	.221
			2	500	29.63	.228
				550	29.39	

[a] Oven temperature at which the plate was heated for 45 min. before counting. [b] Observed number of counts per min. per mg. of solution. [c] Accepted concentration (for each plate) of total uranium in mmoles per 1000 g. of solution.

mum time necessary to insure complete reduction of the uranium. The deviation from a constant equilibrium value became more pronounced as the HF concentration was increased. In run 9, with the highest HF concentration used, values for the number of mmoles of uranium per 1000 g. of solution were observed to be 0.367 and 0.372 after 45 min. and 0.372 and 0.373 after 1 day at 25.0°. One day after returning to 25.0 from 35° the values were 0.355, 0.361, 0.377, 0.365, 0.352 and 0.353. After 3 days the observed values were 0.339, 0.343, and after longer intervals continued to fall even lower. The value of 0.37 was accepted as the equilibrium value for this run.

For each solution the fluoride ion concentration was calculated, using the equilibrium (activity) constants at 25° of Broene and DeVries.[7] Activity coefficients of all neutral species were assumed to be unity. Activity coefficients of all singly charged ions were taken as equal to the mean activity coefficient of perchloric acid, $\gamma = 0.796$ for 0.12 M perchloric acid at 25°.[8]

$$HF \rightleftharpoons H^+ + F^- \qquad K_{HF} = 6.7_1 \times 10^{-4}$$

$$HF + F^- \rightleftharpoons HF_2^- \qquad K_{HF} = 3.92$$

From an approximation of the fluoride ion concentrations, made by ignoring the contribution from the dissolved UF_4 and from the corresponding behavior of the uranium concentration, it became evident that both positively and negatively charged uranium–fluorine complex ions were present. The observed behavior could be explained by assuming the equilibria

$$2UF_4 \cdot 5H_2O \rightleftharpoons 2UF_4^0(aq) + 5H_2O \qquad (1)$$

$$UF_4^0(aq) \rightleftharpoons UF_3^+ + F^- \qquad (2)$$

$$UF_3^+ \rightleftharpoons UF_2^{++} + F^- \qquad (3)$$

$$UF_4^0(aq) + F^- \rightleftharpoons UF_5^- \qquad (4)$$

$$UF_5^- + F^- \rightleftharpoons UF_6^= \qquad (5)$$

with the corresponding equilibrium constants

$$k_1 = [UF_4{}^0{}_{aq}]$$

$$k_2 = \frac{[UF_3{}^+][F^-]}{[UF_4{}^0{}_{aq}]}$$

$$k_3 = \frac{[UF_2{}^{++}][F^-]}{[UF_3{}^+]}$$

$$k_4 = \frac{[UF_5{}^-]}{[UF_4{}^0{}_{aq}][F^-]}$$

$$k_5 = \frac{[UF_6{}^=]}{[UF_5{}^-][F^-]}$$

where [ ] represents the concentration of a given species in moles per 1000 grams of solvent, the solvent being defined as the perchloric–hydrofluoric acid mixture of 0.12 m ionic strength used in each case. Since the corresponding activity coefficients of the various species have not been evaluated, these constants are not independent of the ionic strength but at a constant ionic strength should be independent of the concentration of any given species.

The variation of the total uranium in solution as a function of fluoride ion at constant temperature and ionic strength should then follow the relationship

$$\begin{aligned}\alpha &= [UF_6{}^=][UF_5{}^-] + [UF_4{}^0] + [UF_3{}^+] + [UF_2{}^{++}] \\ &= A[F^-]^2 + B[F^-] + C + D[F^-]^{-1} + E[F^-]^{-2} \quad (6)\end{aligned}$$

where the parameters are so related to the equilibrium constants that $A = k_1k_4k_5$, $B = k_1k_4$, $C = k_1$, $D = k_1k_2$ and $E = k_1k_2k_3$.

An equation of the form 6 above was fitted to five experimental values of α obtained from runs 3, 8, 6, 11 and 9, together with the corresponding approximate values for $[F^-]$ calculated as described above. In the case of run 3, where $\beta = 0$ and therefore all of the fluoride had to come from the ionization of UF_4, as a first approximation a tentative value for $[UF_4{}^0{}_{aq}]$ of 1.0×10^{-4} (just below the lowest observed solubility value) was taken and the assumption made that the remaining uranium was about equally divided between $[UF_3{}^+]$ and $[UF_2{}^{++}]$. The resulting five linear equations were solved for the parameters A, B, C, D and E, and these five approximate values then were used to calculate better approximations for the fluoride ion concentrations in each of the five runs. By a series of successive approximations consistent values for the parameters and fluoride ion concentrations were obtained; those for the parameters and the equilibrium constants calculated are

$$A = 8.3 \times 10^{-1} \qquad k_1 = C = 1.09 \times 10^{-4}$$

$$B = 4.2 \times 10^{-3} \qquad k_2 = D/C = 5.4 \times 10^{-5}$$

$$C = 1.09 \times 10^{-4} \qquad k_3 = E/D = 5.9 \times 10^{-5}$$

$$D = 5.9 \times 10^{-9} \qquad k_4 = B/C = 3.9 \times 10^{1}$$

$$E = 3.5 \times 10^{-13} \qquad k_5 = A/B = 2.0 \times 10^{2}$$

Figure 2 shows a plot of equation 6 with these values for the parameters. In order to cover the

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(7) H. H. Broene and T. DeVries, THIS JOURNAL, **69**, 1644 (1947).

(8) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

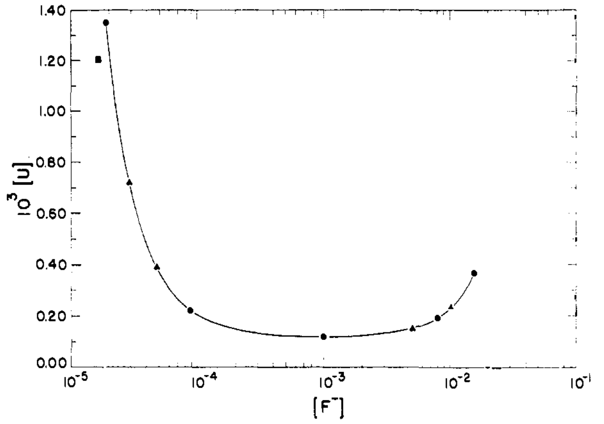

Fig. 2.—The solubility of UF_4 at 25.0° at $\mu = 0.12$ as a function of fluoride ion concentration. Circles represent the five experimental points to which the theoretical curve was fitted. The square represents the value for run no. 1. Triangles represent the remaining experimental points.

whole range of fluoride ion concentrations in sufficient detail, those concentrations are presented on a logarithmic scale.

Table III lists the calculated values for the various experimental runs, including a column of values for α calculated from equation 6 for comparison with observed values.

TABLE III

COMPARISON OF OBSERVED URANIUM CONCENTRATIONS WITH CALCULATED VALUES

Run	μ	[F⁻]	$\alpha_{\text{calcd.}}$ × 10^3	$\alpha_{\text{obsd.}}$ × 10^3
3	0.122	1.92×10^{-5}	1.35	1.35
4	.122	2.53×10^{-5}	0.88	0.72
7	.121	4.82×10^{-5}	.38	.39
8	.121	8.77×10^{-5}	.22	.22
6	.121	9.61×10^{-4}	.12	.12
10	.121	5.00×10^{-3}	.15	.15
11	.121	8.00×10^{-3}	.20	.20
5	.115	9.75×10^{-3}	.23	.22
9	.121	1.54×10^{-2}	.37	.37

For the five runs used in calculating the parameters, the largest and smallest values of α which appeared to be reliable measures of the equilibrium value in each case (expressed as mmoles of U per 1000 g. of solvent) were

Run	3	8	6	11	9
Largest α	1.352	0.224	0.124	0.199	0.378
Smallest α	1.338	0.220	0.117	0.194	0.365

Various combinations of these values were used to recalculate the parameters in order to establish the relationship between the uncertainty in the observed α's and the uncertainty in the parameters. The highest and lowest values which could be thus obtained for the five parameters were

	A	*B*	*C*	*D*	*E*
Highest	9.9×10^{-1}	6.5×10^{-3}	1.16×10^{-4}	6.9×10^{-9}	3.9×10^{-13}
Lowest	6.9×10^{-1}	1.7×10^{-3}	1.03×10^{-4}	4.6×10^{-9}	3.2×10^{-13}

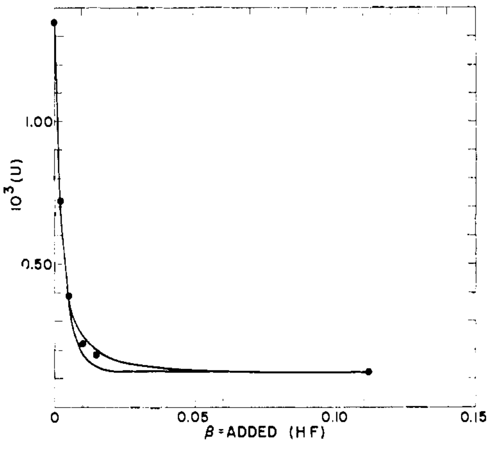

Fig. 3.—α as a function of β in the low fluoride region. The upper curve represents the theoretical behavior if no UF_2^{++} were present; the lower curve shows the theoretical behavior if no UF_3^+ were present; circles show observed values.

Discussion

The interpretation of the results described above falls into two nearly independent parts. In solutions where the calculated fluoride ion concentration was greater than 10^{-3} *m*, the concentration of positively charged complex ions of the type UF_3^+ and UF_2^{++} was negligibly small. Therefore the variation of the total uranium concentration with fluoride ion should have been linear if UF_5^- had been the only negative complex formed. Although as mentioned earlier the experimental difficulties in this region led to slightly greater uncertainties, it is nevertheless certain that the plot of U *vs.* [F⁻] is not linear, and hence uranium complexes containing more than five fluorine atoms probably were present.[9]

In the region of lowest fluoride ion concentrations, on the other hand, concentrations of negative complexes were vanishingly small. Here, too, experimental uncertainties were smaller. But in this region the value of the calculated fluoride ion concentration becomes increasingly sensitive to the relative values used for the parameters *D* and *E*, which are measures of the relative concentrations of UF_3^+ and UF_2^{++}. In this region it is helpful to consider the theoretical variation of α as a function of β, the added HF. Fig. 3 shows such a plot. The upper curve represents the theoretical behavior if no UF_2^{++} were present, but only UF_4^0 and UF_3^+; the lower curve shows the relationship if only UF_2^{++} and UF^0 were present, with no UF_3^+. In both cases the total solubility with $\beta = 0$ was taken to be the observed value of 1.35×10^{-3} *m* as found in run 3 and the value of 0.120×10^{-3} *m* for $\beta = 0.1117$ from run 6. It will be noted that both curves coincide, within the limits of experimental detectability, except for the region $0.006 < \beta < 0.03$. The value obtained in run 8 lies about midway between these

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[9] This reasoning, of course, assumes that the activity coefficient ratio $\gamma_{UF_5^-}/\gamma_{F^-}$ remains constant at a constant ionic strength despite the radical change in the nature of the ionic atmosphere. In order to preclude the possibility of the presence of $UF_6^{=}$ or other complex species, this activity coefficient ratio would have to double in value from run 9 to run 10.

curves. Another run in this region, with $\beta = 0.0150$ also gave an observed $\alpha (0.177 \times 10^{-3} < \alpha < 0.181 \times 10^{-3})$ about midway between the curves, but this value was not reported above because equilibrium was not approached from both sides. These points are shown in Fig. 3 and indicate that both UF_2^{++} and UF_3^{+} are present.

It may well be that other ionic species such as UF^{+3} and U^{+4} also exist in these solutions. However, if they do exist, they are present in quantities so small as to be undetected by the methods of this investigation, and postulating their existence is not necessary to fit the observed data to a smooth curve.

Acknowledgments.—The authors wish to express their appreciation to E. R. Jette, R. D. Baker and R. J. Bard, under whose general direction this work was done, for many helpful discussions and suggestions. They are also grateful to Maynard Smith of this Laboratory for all polarography, to E. Staritzky for optical verifications, to C. J. D'Agostino for experimental assistance and to G. Scatchard, G. Seaborg and J. J. Katz for helpful suggestions.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS TECHNOLOGICAL COLLEGE, LUBBOCK, TEXAS]

The Chemistry of the Solvated Metal Chelates. II. The Uranium(VI), Thorium(IV) and Scandium(III) 2-Methyl-8-quinolinol Metal Chelates[1,2]

BY JAMES H. VAN TASSEL AND WESLEY W. WENDLANDT

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The 2-methyl-8-quinolinol chelates of thorium(IV), scandium(III) and uranium(VI) were studied by chemical, thermogravimetric and calorimetric methods and infrared spectroscopy. The heat of solvation, ΔH_4, for the reaction

$$M(C_{10}H_8NO)_n(s) + C_{10}H_8NOH(s) = M(C_{10}H_8NO)_n \cdot C_{10}H_6NOH(s)$$

was determined for the thorium and uranium chelates and found to be 2.5 ± 0.5 and −2.9 ± 0.5 kcal. mole^{-1}, respectively. It was possible to prepare the unsolvated scandium and uranium chelates by vacuum sublimation techniques and also the previously unreported solvated thorium chelate. There was little difference between the infrared spectra of the solvated and unsolvated metal chelates.

Introduction

2-Methyl-8-quinolinol (2-methyloxine) forms five membered ring metal chelates with a number of metal ions which are quite similar in properties to the chelates formed by 8-quinolinol.[3] The normal formula for the metal chelates is $M(C_{10}H_8NO)_n$, where M is a metal ion of oxidation number n. However, with uranium (VI) and scandium (III), complexes having the formulas, $UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_8NOH$ and $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_8NOH$, are obtained.[4] The extra molecule of chelating agent is held in the crystal lattice by forces of an unknown magnitude. The 2-methyl-8-quinolinol chelate with thorium(IV) does not contain an extra solvate molecule; this is in contrast to the corresponding metal chelate with 8-quinolinol.[5] Because of the excellent thermal properties of the 4:1 thorium 2-methyl-8-quinolinol chelate, it has been recommended as an organic precipitant for that ion.[6]

The purpose of this investigation is to study the nature of the interaction between the solvate molecules and the metal chelates. A previous study[7] has shown that the heat of solvation between 8-quinolinol and the thorium(IV) and uranium(VI) chelates was from −4.9 to −6.5 kcal. mole^{-1}. It was of interest to determine the effect of the methyl group in the 2-position on the heat of solvation of the 2-methyl-8-quinolinol metal chelates. The methyl group in this position is responsible for the non-formation of an aluminum chelate with 2-methyl-8-quinolinol, the effect being attributed to steric hindrance.[8]

Experimental

Reagents.—2-Methyl-8-quinolinol was obtained from the Aldrich Chemical Co., Milwaukee, Wisc. It was purified before use by recrystallization from an ethanol-water mixture; the resulting product had a m.p. of 72–73°. Scandium oxide, 99.8% purity, was obtained from A. D. Mackay Inc., New York, N.Y.; thorium nitrate 4-hydrate from the Lindsay Chemical Co., West Chicago, Ill.; uranium nitrate 6-hydrate from Merck and Co., Rahway, N.J.

A solution of 3.00 ± 0.03 N hydrochloric acid was prepared and standardized against a carbonate-free sodium hydroxide solution.

All other chemicals were of C.P. quality.

Calorimeter.—The heat of solution calorimeter has previously been described.[7] It was modified slightly in that the unbalance potential from the thermister bridge was amplified by a Honeywell, Model 2HLA-7, low-level d.c. amplifier and then recorded on a Varian, Model G-10, strip-chart potentiometric recorder. A chart speed of $^5/_8$ in. per min. was used to record the bridge output. The procedure for the measurements was the same as previously described.[7]

Thermobalance.—The thermobalance has previously been described.[9] Sample sizes ranged in weight from 80–100 mg. and were run in duplicate or triplicate. A linear heating rate of 6.6° per min. was employed on all runs.

Infrared Studies.—The infrared absorption spectra were obtained with a Perkin-Elmer Model 112 single beam double pass instrument. The fused KBr pellet technique

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(1) Taken in part from the Ph.D. thesis of J. H. Van Tassel, Texas Technological College, August, 1959.

(2) Presented at the 15th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, Louisiana, December 3–5, 1959.

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