Potentiometric and Spectrophotometric Studies of Fluoride Complexes of Uranium(IV)

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The stability constants and the molar extinction coefficients of uranium(IV) fluoride complexes were determined in aqueous solutions containing 1 M $(Na^+ + H^+)Cl^-$ as a constant ionic medium at 25 °C. The emf data obtained by the use of a fluoride-ion-selective electrode were explained in terms of the formation of a series of mononuclear complexes, UF^{3+}, UF_2^{2+}, UF_3^+, and UF_4, with stability constants $\beta_1 = (2.2 \pm 0.13) \times 10^7$, $\beta_2 = (1.33 \pm 0.05) \times 10^{13}$, $\beta_3 = (2.9 \pm 0.5) \times 10^{17}$, and $\beta_4 = (6 \pm 1) \times 10^{21}$ respectively. Using these values for β's the spectra observed in the 350—700 nm region were analyzed by means of a computer in order to estimate the molar extinction coefficients of each uranium(IV) fluoride complex species.

The visible and ultraviolet spectra of uranium(IV) have thus far been investigated in crystal, gases, and aqueous solutions. Conway1) measured the absorption spectra of UF, dissolved in a matrix of CaF_2 and assigned all the absorption peaks to the transition caused by two 5f electrons. Pappalardo and Jφrgensen2) studied the absorption spectra of uranium(IV) in the octahedral coordination. Satten *et al.*3) calculated the energy parameters of $5f^2$ electrons in crystals.

The absorption spectra of aquated uranium(IV) ions in $HClO_4$4) and $DClO_4$5) solutions were reported. Spectrophotometric studies of uranium(IV) fluoride complexes were carried out by Stein *et al.*6) in 1 M $HClO_4$ and 1 M H_2SO_4 solutions over the range of 300—1300 nm. They prepared complex salts $UFSO_4(HSO_4)\cdot 2H_2O$, $UF_2SO_4\cdot 2H_2O$, and $(UF_3)_2SO_4\cdot 4H_2O$ and discussed the infrared spectra and X-ray powder patterns. Baran and Tympl7) measured the absorption spectra of the hydroxo and carbonato complexes of uranium(IV).

In solutions, the absorption spectra usually change in band shape and in position with the change in ligand concentration, because several species can coexist in a solution and because the mole fraction of each species varies with the ligand concentration.

A potentiometric titration is one of the most accurate methods for studying chemical equilibria in solution. Recently-developed fluoride-ion-selective electrodes are very useful for studying fluoride complexes in solution. Uranium(IV) fluoride complexes were studied by means of the fluoride-ion-selective electrodes by Norén8) in a 4 M $HClO_4$ solution and by Grenthe and Varfeldt9) in a mixture of 3.4 M $NaClO_4$ and 0.6 M $HClO_4$ and the formations of UF^{3+}, UF_2^{2+}, and UF_3^+ complexes have been reported. The electronic spectra of these species, however, have not yet been measured.

In the present study, the stability constants of uranium(IV) fluoride complexes were determined in a 1 M $(Na^+ + H^+)Cl^-$ solution by potentiometry with a fluoride-ion-selective electrode, and on the basis of these constants the spectrophotometric data were analyzed by means of a computer in order to estimate the molar extinction coefficients of each uranium(IV) fluoride complex species.

Experimental

Reagents. The uranium(IV) chloride used was prepared by the following method. The uranium metal was dissolved in dilute hydrochloric acid and then treated with nitric acid. The uranyl nitrate thus prepared was recrystallized twice from water and then converted to ammonium diuranate by the addition of ammonia. The ammonium diuranate precipitates were washed with water, dried under an infrared lamp, and decomposed to triuranium octoxide, U_3O_8, by heating at 900 °C for about 6 hr. The test solutions were prepared by the electrolytic reduction of UO_2Cl_2 solutions which had been prepared by dissolving U_3O_8 in hydrochloric acid.

The other chemicals used were of a reagent grade. Sodium fluoride was once recrystallized from water and dried in an electric furnace at 120 °C for 16 hr.

Apparatus. The test solutions containing fluoride ions were stored in polyethylene bottles. A fluoride-ion-selective electrode (Orion 94–09) was used for the determination of the free-fluoride-ion concentration. A specific-ion meter (Orion model 404) was employed to measure the potential of the fluoride-ion-selective electrode against a saturated calomel electrode used as reference.

The visible spectra were measured by means of an MPS 50L (Shimadzu Seisakusho Co. Ltd.) double-beam spectrophotometer, using a quartz cell 1.00 cm thick.

Measurements. In the solution used, the electrode exhibited Nernst behavior throughout the region of the free-fluoride-ion concentration of $10^{-4} \geq [F^-] \geq 10^{-6}$ M. The constant ionic medium was kept at 1 M with sodium chloride. A back-titration technique starting at a high fluoride-ion concentration was employed in the present experiment in order to avoid the formation of precipitates during the titration and the corrosion of burets. A solution containing C_U M uranium(IV) and C_F M fluoride ions was titrated with a solution containing C_U M uranium(IV) ions to keep the total concentration of uranium(IV) constant (C_U) throughout the titration. The concentration of uranium(IV) was gravimetrically determined in the form of U_3O_8. Uranium-(IV) was gradually oxidized to uranium (VI) even in a solution under an atmosphere of nitrogen. To avoid errors caused by oxidation, the test solution was prepared immediately before each titration.

The test solutions for spectrophotometric measurements were prepared under the same ionic medium conditions as in the emf measurements.

Results and Discussion

Potentiometric Measurements. Formation curves at different total concentrations of uranium(IV) are shown in Fig. 1. The experimental results are discribed in terms of n_{exp}, the average number of fluoride ions

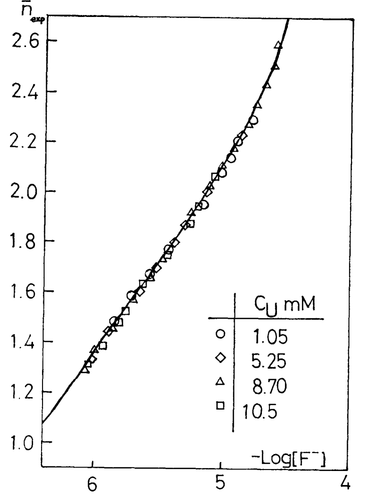

Fig. 1. Average number, $\bar{n}_{exp}$, of F^- bound per uranium(IV), as a function of $-\log$ [F^-]. The curve was calculated using the constants obtained.

bound to the uranium(IV) ion, as a function of $-\log$[F^-]. Potentiometric measurements were carried out in the region where the fluoride-ion concentration was larger than 10^{-6} M, where the fluoride-ion-selective electrode exhibited Nernst behavior and a quick response to the change in the fluoride-ion concentration. Since the hydrogen fluoride complexes, HF and HF_2^-, are formed in an acidic solution ($[H^+] \gtrsim 0.1$ M),[10,11] $\bar{n}_{exp}$ was calculated by means of the equation:

$$\bar{n}_{exp} = (C_F - [F^-] - [HF] - 2[HF_2^-])/C_U$$
$$= (C_F - f - K_{11}hf - 2K_{11}K_{12}hf^2)/C_U \qquad (1)$$

where C_F, C_U, f, and h stands for the total fluoride, total uranium(IV), free-fluoride-ion, and free-hydrogen-ion concentrations respectively, and where K_{11} and K_{12} denote the step-by-step stability constants of these reactions:

$$H^+ + F^- = HF;\ K_{11} = [HF]/[H^+][F^-] \qquad (2)$$

$$HF + F^- = HF_2^-;\ K_{12} = [HF_2^-]/[HF][F^-] \qquad (2')$$

The values of K_{11} and K_{12} are given as 6.93×10^2 and 3.2 respectively.[10]

As is shown in Fig. 1, the formation curves are independent of the uranium(IV) concentration. This fact indicates the formation of a series of mononuclear complexes. The approximate values of the stability constants of the complexes were estimated by the graphical method as has been described by Rossotti and Rossotti.[12] The formation function:

$$\bar{n}_{exp} = \sum n\beta_n f^n/(1+\sum\beta_n f^n) \qquad (3)$$

can be rearranged as follows:

$$\sum_{i=0}^{n-1}\left(\frac{\bar{n}-i}{n-\bar{n}}\right)\beta_i f^{i-n} = \beta_n + \sum_{i=n+1}^{N}\left(\frac{i-\bar{n}}{n-\bar{n}}\right)\beta_i f^{i-n} \qquad (4)$$

where β_n denotes the cumulative stability constant of this reaction:

$$U^{4+} + nF^- = UF_n^{4-n};\ \beta_n = [UF_n^{4-n}]/[U^{4+}][F^-]^n \qquad (5)$$

The initial part of the plot of $\sum_{i=0}^{n-1}(\bar{n}-i)\beta_i f^{i-n}/(n-\bar{n})$ against $(i-\bar{n})f/(n+1-\bar{n})$ gives a straight line with an intercept of β_n and a slope of β_{n+1}. The procedure is continued until the plot of $\sum_{i=0}^{n-1}(\bar{n}-i)\beta_i f^{i-n}/(n-\bar{n})$ against $(i-\bar{n})f/(n+1-\bar{n})$ becomes horizontal. In our case, the procedure could be carried out until $n=4$, the plot was so spread that the formation of UF_5^- was not conclusive.

If we assume the formation of four complexes, UF^{3+}, UF_2^{2+}, UF_3^+, and UF_4, the mole balances for uranium(IV), fluoride, and hydrogen ions can be expressed by the following equations:

$$C_U = [U^{4+}] + [UF^{3+}] + [UF_2^{2+}] + [UF_3^+] + [UF_4]$$
$$= u(1+\sum_{n=1}^{4}\beta_n f^n) \qquad (6)$$

$$C_F = [F^-] + [HF] + 2[HF_2^-] + [UF^{3+}] + 2[UF_2^{3+}]$$
$$+ 3[UF_3^+] + 4[UF_4]$$
$$= f + K_{11}hf + 2K_{11}K_{12}hf^2 + u\sum_{n=1}^{4}n\beta_n f^n \qquad (7)$$

$$C_H = [H^+] + [HF] + [HF_2^-]$$
$$= h + K_{11}hf + K_{11}K_{12}hf^2 \qquad (8)$$

where u represents the free-uranium(IV)-ion concentration. n_{calcd} is given by the following equation:

$$\bar{n}_{calcd} = \sum_{n=1}^{4}n\beta_n f^n/(1+\sum_{n=1}^{4}\beta_n f^n) \qquad (9)$$

Finally, the error-square sum, $U = \sum(1-\bar{n}_{exp}/\bar{n}_{calcd})^2$ was minimized in order to obtain a set of the best-fit values of the stability constants by the least-squares method with the help of an electronic computer (HITAC 8500 and 8700). The formation curve was calculated using the four stability constants thus obtained. The calculated formation curve well explains the experimental points, as Fig. 1 shows. If only three complexes, UF^{3+}, UF_2^{2+}, and UF_3^+, were taken into consideration, the formation curve deviated from the experimental points at high $\bar{n}$ values ($\bar{n} \geq 2.2$). Since the calculation on the assumption of the formation of the UF_5^- complex in addition to the other four did not reduce the error-square sum remarkably, it may be concluded that there is very little mole fraction of the UF_5^- complex, if any, in this system. The final values of the stability constants obtained for the four uranium(IV) fluoride complexes, UF^{3+}, UF_2^{2+}, UF_3^+, and UF_4, are $\beta_1 = (2.2 \pm 0.13) \times 10^7$, $\beta_2 = (1.33 \pm 0.05) \times 10^{13}$, $\beta_3 = (2.9 \pm 0.5) \times 10^{17}$, and $\beta_4 = (6 \pm 1) \times 10^{21}$ respectively. They are listed in Table 1, together with the values reported in Ref. 8 and 9 and those obtained by solubility measurements by Savage and Browne.[13] As for β_2 and β_3, our results agreed well with Ref. 8, while for β_4 they agreed fairly well with Ref. 13. In Fig. 2, we show the distribution of the species of uranium(IV) fluoride complexes.

Mesmer and Baes[14] have studied a general correlation for the step-by-step stability constants of the fluoride complexes of a large number of metal ions and reported that the $\Delta\log K_n$ values can be well represented by:

$$\Delta \log K_n = -\alpha\Delta n \qquad (10)$$

where K_n is the step-by-step stability constant ($=\beta_n/\beta_{n-1}$) and where n is the number of fluoride ions in the complex formed. They have concluded that the best-fitting value for α is 1.1. The $\Delta\log K_n$ values for uranium(IV) are plotted against n, together with those for other metals such as uranium(VI),[10] thorium(IV),[8,16,17] hafnium(IV),[18] and beryllium(II).[14] The

Table 1. The stability constants of uranium(IV) fluoride complexes

Reference	Medium	Temp.	β_1^*	β_2^*	β_3^*	β_4^*
This work	1 M $(Na^+ + H^+)Cl^-$	25 °C	$(3.1 \pm 0.3) \times 10^4$	$(2.8 \pm 0.1) \times 10^7$	$(9 \pm 1) \times 10^8$	$(1.3 \pm 0.5) \times 10^{10}$
Ref. 8	4 M $HClO_4$	20 °C	$(8.8 \pm 0.2) \times 10^4$	$(3.3 \pm 0.2) \times 10^7$	$(8 \pm 1) \times 10^8$	—
Ref. 9	3.4 M $NaClO_4$ 0.6 M $HClO_4$	25 °C	$(2.34 \pm 0.06) \times 10^5$	$(1.94 \pm 0.04) \times 10^8$	$(2.8 \pm 0.2) \times 10^9$	—
Ref. 13	0.12 M $HClO_4$	25 °C	—	—	2.5×10^{10}	2.8×10^{10}

Uncertainties of the stability constants were estimated as 3σ where σ denotes the standared deviation. The results are described in terms of β_p^*, $\beta_p^* = \beta_p / K_{11}{}^p$, for comparison with other data. β_p^* is the over-all stability constants of the following reaction,

$$U^{4+} + pHF = UF_p{}^{4-p} + pH^+;\ \beta_p^* = [UF_p{}^{4-p}][H^+]^p / [U^{4+}][HF]^p$$

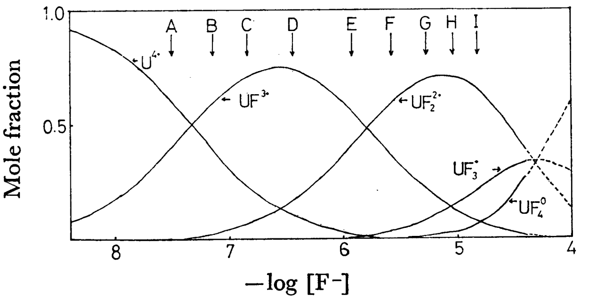

Fig. 2. The distribution of species of uranium(IV) fluoride complexes calculated using the stability constants obtained. Arrows (A-I) indicate compositions of species and free fluoride ion concentrations used for spectrophotometric measurements.

same α value of 1.1 is obtained for uranium(VI) and beryllium(II) fluoride complexes. A little larger value of 1.5 is found for the uranium(IV) and thorium(IV) fluoride complexes, with the exception of UF_4, the step-by-step stability constant of UF_4 being larger than would be expected from Eq. (10) on the assumption that $\alpha = 1.5$. The plots for thorium(IV) fluoride complexes in different ionic media give the same slope.

Spectrophotometric Measurements. Without the fluoride ion, the spectra of the aquated uranium(IV) ion were measured in a 1 M HCl solution with various uranium(IV) concentrations in the 350—700 nm region, where the formation of chloro complexes of uranium(IV) is negligible.[15] The molar extinction coefficients of the aquated uranium(IV) ion in this region are shown in Fig. 4, together with those of UOH^{3+} as measured by Baran and Tympl.[7] The spectra of the uranium(IV) fluoride complexes were measured in the same ionic media as those used for the potentiometric titrations. The 9 fluoride-ion concentrations at which the spectra have been measured are marked with arrows (A-I) in Fig. 2.

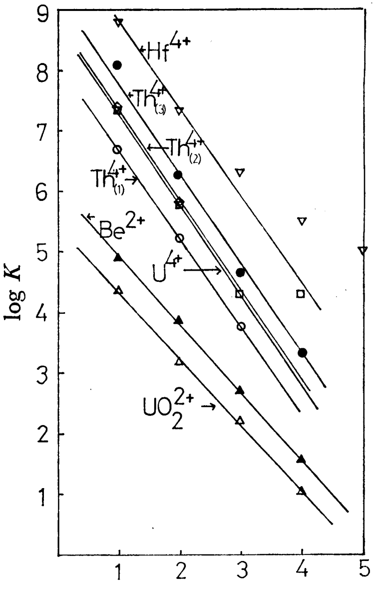

Fig. 3. The correlation of stepwise formation constants with n, the number of fluoride ion in the complex.

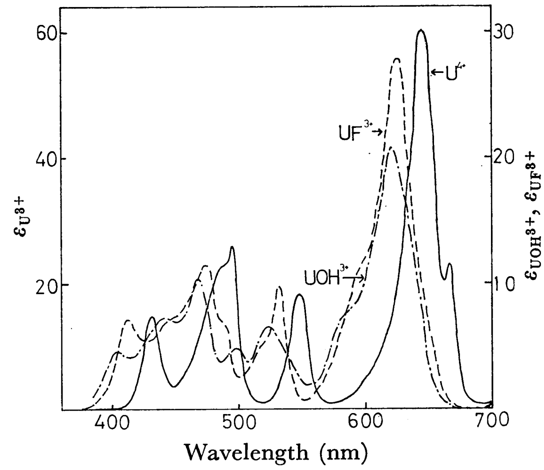

Fig. 4. The spectra of the aquated U^{4+} and UOH^{3+} ions and the calculated spectrum of UF^{3+}.

Since four mononuclear complexes of uranium(IV) fluoride were found by the potentiometric measurements, the total absorbance, A, in solution can be expressed as follows:

$$\begin{aligned} A &= \varepsilon_0[U^{4+}] + \varepsilon_1[UF^{3+}] + \varepsilon_2[UF_2{}^{2+}] \\ &\quad + \varepsilon_3[UF_3{}^+] + \varepsilon_4[UF_4] \\ &= u\sum_{n=0}^{4} \varepsilon_n \beta_n f^n \end{aligned} \tag{11}$$

where ε_n denotes the molar extinction coefficient of the relevant species and where β_0 is unity. Nine sets of data obtained by spectrophotometric measurements were used for the estimation of the molar extinction coefficients of the uranium(IV) fluoride complexes. The value of ε_0 at a given wavelength was adopted from the results in Fig. 4 (the spectrum of U^{4+}). In order to avoid errors in the calculation at a given uranium(IV) concentration, the total absorbance of the solution at the absorption maximum (600—650 nm) was kept approximately constant (about 0.8) by varying the uranium(IV) concentration from 0.023 to 0.047 M. The values of ε's of the complexes can be calculated by solving Eqs. (6), (7), (8), and (11) at any point in the 350—700 nm region. The most suitable values of ε's were obtained by minimizing the error-square sum, $U=\sum(A_{\text{calcd}}-A_{\text{exp}})^2$, at given wavelength. The calculated molar extinction coefficients of the UF^{3+} complex are graphically shown in Fig. 4, while those of UF_2^{2+} and UF_3^+ are shown in Fig. 5. Using these values for ε_n, the total absorbance was calculated and compared with the observed absorbance. Some typical results of the comparison are shown in Fig. 6. This good agreement between the observed and calculated spectra may support the above-mentioned analysis and may make it possible to discuss ε_n a little further.

The spectrum of UOH^{3+}, as measured by differential spectroscopy by Baran and Tympl,[7] is depicted for comparison in Fig. 4. It may be seen from Fig. 4 that, as a rule, the absorption peaks of the aquated U^{4+} ion shift to a wavelength shorter by 20—25 nm when a water molecule in the aquated U^{4+} ion is replaced with F^- or OH^- ions. Furthermore, the spectrum of UOH^{3+} has small absorption peaks at about 430 and 500 nm and a shoulder at 580 nm, while the spectrum of UF^{3+} has shoulders at about 430, 490, 520, and 595 nm. These small absorption peaks and shoulders of UOH^{3+} and UF^{3+} do not correspond to any peaks of the aquated U^{4+}. They may be supposed to be caused by changes in the ligand-field symmetry of UOH^{3+} and UF^{3+}. The hydroxyl ion may have a larger effect on the splitting of the degenerated states of $5f^2$ electrons in uranium(IV) than does the fluoride ion.

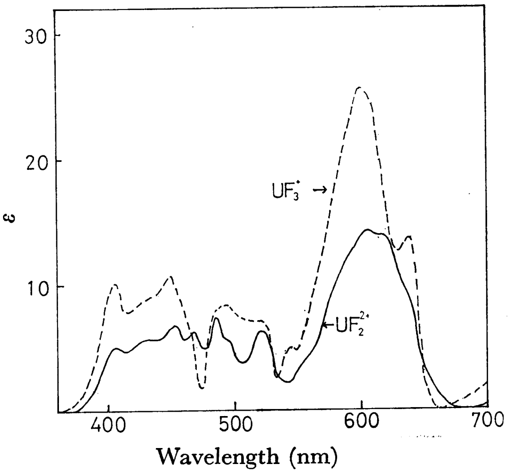

Fig. 5. The calculated spectra of UF_2^{2+} and UF_3^+.

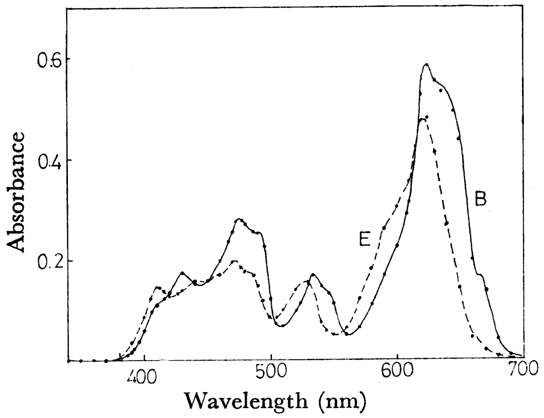

Fig. 6. Typical absorption spectra of uranium(IV) fluoride complexes. The calculated total absorbances are represented by dots. Solid and broken lines show measured absorption spectra of solutions with the following compositions of species.

(B) U^{4+}: 38.7%, UF^{3+}: 58.8%, UF_2^{3+}: 2.5% (indicated by arrow B in Fig. 2)

(E) U_4^+: 2%. UF^{3+}: 54.8%, UF_2^{2+}: 42%, UF_3^+: 1.2% (arrow E)

As for the spectrum of UF_2^{2+}, the peaks shift by about 10 nm to a wavelength shorter than those of UF^{3+}, and several additional peaks appear in the 400—500 nm region. The large absorption band at about 610 nm becomes weaker in intensity (about half of that of UF^{3+}) and broader in width.

Since the mole fraction of UF_3^+ is, at most, 35%, much less than those of UF^{3+} (75%) and UF_2^{2+} (70%), the calculated spectrum of UF_3^+ is uncertain compared with those of UF^{3+} and UF_2^{2+}. The absorption peaks of UF_3^+ also seem to shift to a shorter wavelength, but become stronger in intensity than those of UF_2^{2+}, even if uncertainities in calculation are considered.

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