Complex Formation in the U(VI)–OH⁻–F⁻ System

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Complex formation in the ternary system U(VI)–OH⁻–F⁻ has been studied in a 3.00 M $NaClO_4$ ionic medium. Only binary complexes, $(UO_2)_2(OH)_2^{2+}$ (log $\beta_{2,2}^* = -5.98 \pm 0.02$); $(UO_2)_3(OH)_5^+$ (log $\beta_{3,5}^* = -16.23 \pm 0.05$); $UO_2F_n^{2-n}$ (log $\beta_n = 4.86 \pm 0.02$, 8.62 ± 0.04, 11.71 ± 0.06 and 13.78 ± 0.08, respectively, for $n = 1$–4), were formed. The equilibrium constants refer to 25°C. By combining the equilibrium data in 3.00 M $NaClO_4$ with previously reported data obtained in 1.00 M $NaClO_4$, the medium dependence of the equilibrium constants has been estimated using the specific ion interaction model of Brønsted, Guggenheim and Scatchard. By using ¹⁹F NMR spectroscopy it was possible to demonstrate the formation of $UO_2F_5^{3-}$, with the formation constant $K_5 \approx 3$ M⁻¹, at −4°C for the reaction $UO_2F_4^{2-} + F^- \rightleftharpoons UO_2F_5^{3-}$. The chemical shifts at −4°C for the various $UO_2F_n^{2-n}$ complexes were 165, 143, 123, 104.5 and 83 ppm for $n = 1$–5, respectively (referred to 0.1 M NaF in 3.00 M $NaClO_4$ at 25°C). At higher temperatures there was a significant exchange broadening of the spectra. There was no evidence for the formation of ternary complexes $(UO_2)_p(OH)_q F_r$ in the concentration available for experimental study [this was limited owing to precipitation of $UO_2(OH)_2$ (s)]. From the NMR data it is possible to estimate an upper limit of the equilibrium constants of $(UO_2)_2(OH)_2 F^+$ and $(UO_2)_3(OH)_5 F$, if such complexes are formed.

The binary systems U(VI)–F⁻ and U(VI)–OH⁻ have been extensively studied; cf. Grenthe et al.[1] for a recent review. The fluoride system is mononuclear, and the equilibrium constants for the species $UO_2F_n^{2-n}$, $n = 1$–4, have previously been determined[1] using different experimental methods. The hydroxide complexes are mainly polynuclear even at very low total concentrations of U(VI).[1] Both fluoride and hydroxide are excellent bridging ligands in the solid state;[2,3] however, in solution only the hydroxide forms bridges.[4]

In a previous study of the Be²⁺–F⁻OH⁻ system[4] we observed the formation of ternary complexes through the replacement of coordinated water in the polynuclear hydroxide complexes with fluoride. The equilibrium constants for the binding of fluoride to the Be(II)–hydroxide complexes were about a factor of ten smaller than the equilibrium constant for the corresponding mononuclear reactions, e.g. Be²⁺ + F⁻ ⇌ BeF⁺. This study[4] also illustrated the practical utility of ¹⁹F NMR for the study of equilibria in fluoride systems, both for the identification of new species and for the determination of equilibrium constants. One reason for this is that the large chemical shift differences observed between the various complexes result in smaller complications due to exchange between the different fluoride sites.

In the present study we explore two aspects of the U(VI)–F⁻–OH⁻ system: (i) the maximum coordination number of fluoride in the binary system U(VI)–F⁻ and (ii) the possible formation of ternary complexes, analogous to the ones previously found in the Be²⁺–F⁻–OH⁻ system. The coordination number of UO_2^{2+} in the solid state is five or six, with the donor atoms in a plane perpendicular to the linear UO_2^{2+} ion. With monodentate ligands F⁻ in $K_3UO_2F_5$,[5] H_2O in $[UO_2(H_2O)_5](ClO_4)_2(H_2O)_2$[6] and NCS⁻ in $Cs_3[UO_2(NCS)_5]$[7] the coordination polyhedron is a pentagonal bipyramid. With bidentate ligands CO_3^{2-} in $(NH_4)_4[UO_2(CO_3)_3]$,[8] and NO_3^- in $Rb[UO_2(NO_3)_3]$[9] a hexagonal bipyramid is formed. The same coordination also seems possible in solution, as indicated by NMR studies of the aqua complex in a mixed acetone–water solvent,[10–12] and by the stoichiometry, NMR characteristics and X-ray scattering of U(VI) carbonate complexes.[13]

The complex $UO_2F_5^{3-}$ has not been observed in solution, probably owing to difficulties in identifying it using standard potentiometric methods at the high concentration of fluoride necessary for its formation. NMR is often a superior method for the detection of complexes which require very high ligand concentrations in order that they may be formed.[14]

The present study of ternary complexes is complicated by the formation of sparingly soluble $UO_2(OH)_2(s)$,

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which restricts the study to smaller concentration ranges in H^+ and $U(VI)$ than in the previous study of the corresponding $Be(II)$ system.

Experimental

Potentiometric data. The experiments were carried out as titrations by varying the fluoride concentration in solutions were the total concentration of $U(VI)$ was kept constant. The concentrations of $[H^+]$ and $[F^-]$ were measured in cell (I) without a liquid junction,

$$- Ag \,|TS|\, H^+ \qquad (I)$$

F^- electrodes, by using a glass electrode (E_g) and a fluoride electrode (E_f), respectively. The test solution had the following general composition:
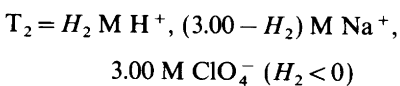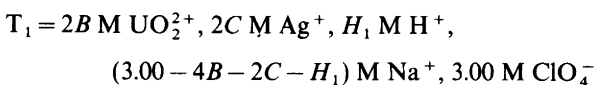
TS: A M F^-, B M UO_2^{2+}, C M Ag^+, H M H^+,

$$(3.00 + A - 2B - C - H)\, M\, Na^+, 3.00\, M\, ClO_4^-,$$
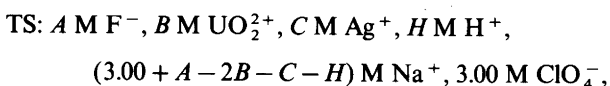
where A, B, C and H are accurately known analytical concentrations, varied in the experimental titration procedure. The EMF, E_g and E_f, are given by eqns. (1) and (2), where h and a represent the equilibrium concentrations

$$E_g = E_g^\circ - 59.16 \log C + 59.16 \log h \qquad (1)$$

$$E_f = E_f^\circ - 59.16 \log C + 59.16 \log a \qquad (2)$$

of H^+ and F^-, respectively.

Each experiment was started by transferring an accurately known volume of solution TS (with $A = 0$, and H sufficiently large to avoid hydrolysis) into the titration vessel. In a first set of experiments the binary system $U(VI)-H_2O$ was studied by adding equal volumes of the titrant solutions T_1 and T_2.
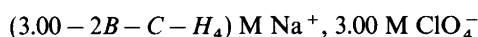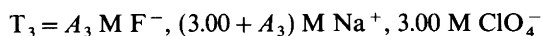
$$T_1 = 2B\, M\, UO_2^{2+}, 2C\, M\, Ag^+, H_1\, M\, H^+,$$

$$(3.00 - 4B - 2C - H_1)\, M\, Na^+, 3.00\, M\, ClO_4^-$$

$$T_2 = H_2\, M\, H^+, (3.00 - H_2)\, M\, Na^+,$$

$$3.00\, M\, ClO_4^-\; (H_2 < 0)$$

In this way H could be decreased in the test solution while keeping the analytical total concentrations of Ag^+ and UO_2^{2+} constant. The electrodes were calibrated by using the Gran method, as described in previous communications.[4]

In a second set of titrations the ternary system $U(VI)-H_2O - F^-$ was studied using data for $E_f(A)_{B,h}$. (Data at constant B and h are most convenient for the equilibrium analysis of this system.) By using a set of four burettes it was possible to collect data at approximately constant values of $-\log[H^+]$ in each titration series. The

Table 1. Survey of $-\log h(H)_B$ data employed for the evaluation of UO_2^{2+} hydrolytic equilibria, given as $-\log h$ followed by H in parentheses.

$B = 0.001$ M

(a)	2.294	(0.00508)	2.343	(0.00453)	2.395	(0.00403)
	2.449	(0.00355)	2.507	(0.00311)	2.568	(0.00270)
	2.635	(0.00232)	2.708	(0.00196)	2.790	(0.00162)
	2.885	(0.00130)	2.998	(0.00100)	3.064	(0.00086)
	3.140	(0.00072)	3.229	(0.00058)	3.336	(0.00045)
	3.468	(0.00032)	3.631	(0.00020)	3.811	(0.00008)
	3.971	(−0.00004)	4.094	(−0.00016)	4.188	(−0.00027)
	4.264	(−0.00038)	4.330	(−0.00049)	4.390	(−0.00060)
	4.446	(−0.00070)	4.484	(−0.00077)		
(b)	2.294	(0.00598)	2.344	(0.00453)	2.423	(0.00378)
	2.508	(0.00310)	2.603	(0.00249)	2.711	(00194)

$B = 0.003$ M

1.822	(0.01506)	1.919	(0.01206)	1.990	(0.01024)
2.068	(0.00855)	2.156	(0.00697)	2.259	(0.00550)
2.385	(0.00412)	2.548	(0.00283)	2.791	(0.00161)
2.980	(0.00103)	3.274	(0.00047)	3.642	(−0.00008)
3.881	(−0.00062)	4.035	(−0.00113)	4.151	(−0.00164)
4.251	(−0.00213)	4.345	(−0.00260)		

$B = 0.008$ M

(a)	1.522	(0.03007)	1.672	(0.02127)	1.761	(0.01736)
	1.863	(0.01372)	1.986	(0.01033)	2.145	(0.00716)
	2.376	(0.00420)	2.553	(0.00278)	4.410	(−0.00964)
(b)	1.522	(0.03007)	1.592	(0.02561)	1.668	(0.02149)
	1.754	(0.01762)	1.851	(0.01408)	1.968	(0.01075)
	2.117	(0.00763)	2.324	(0.00474)	2.699	(0.00197)
	3.469	(−0.00062)	3.688	(−0.00185)	3.836	(−0.00306)
	3.950	(−0.00422)	4.408	(−0.00536)	4.136	(−0.00646)
	4.257	(−0.00796)	4.381	(−0.00936)		
(c)	1.522	(0.03007)	1.590	(0.02569)	1.668	(0.02147)
	1.754	(0.01763)	1.852	(0.01406)	1.970	(0.01072)
	2.122	(0.00754)	2.332	(0.00465)	2.707	(0.00193)
	3.090	(0.00061)	3.479	(−0.00066)	3.695	(−0.00190)
	3.841	(−0.00310)	3.912	(−0.00381)		

$B = 0.010$ M

1.695	(0.02020)	1.736	(0.01838)	1.779	(0.01663)
1.851	(0.01410)	1.929	(0.01176)	2.115	(0.00768)
2.324	(0.00473)	2.524	(0.00297)	2.740	(0.00175)
2.924	(0.00104)	3.266	(−0.00011)	3.941	(−0.00122)
3.685	(−0.00273)	3.838	(−0.00438)	3.983	(−0.00633)
4.127	(−0.00853)	4.337	(−0.01158)		

$B = 0.025$ M

(a)	1.124	(0.07510)	1.177	(0.06649)	1.292	(0.05110)
	1.423	(0.03776)	1.584	(0.02609)	1.739	(0.01825)
	1.955	(0.01108)	2.341	(0.00449)	2.911	(0.00040)
	3.354	(−0.00424)	3.537	(−0.00789)	3.672	(−0.01136)
	3.782	(−0.01466)	3.902	(−0.01873)		
(b)	1.124	(0.07510)	1.191	(0.06445)	1.264	(0.05439)
	1.343	(0.04540)	1.430	(0.03717)	1.529	(0.02961)
	1.645	(0.02263)	1.791	(0.01617)	1.991	(0.01018)
	2.330	(0.00461)	2.823	(0.00094)	3.156	(−0.00158)
	3.341	(−0.00402)	3.469	(−0.00638)	3.570	(−0.00866)
	3.623	(−0.01000)				

$B = 0.075$ M

1.125	(0.07506)	1.219	(0.06037)	1.328	(0.04703)
1.458	(0.03485)	1.625	(0.02370)	1.869	(0.01344)
2.341	(0.00399)	2.887	(−0.00477)	3.056	(−0.01052)
3.172	(−0.01598)	3.264	(−0.02118)	3.361	(−0.02751)
3.476	(−0.03600)	3.597	(−0.04609)		

additional titrant solutions, T_3 and T_4, had the following compositions.

$$T_3 = A_3 \text{ M F}^-, (3.00 + A_3) \text{ M Na}^+, 3.00 \text{ M ClO}_4^-$$

$$T_4 = B \text{ M UO}_2^{2+}, C \text{ M Ag}^+, H_4 \text{ M H}^+,$$

$$(3.00 - 2B - C - H_4) \text{ M Na}^+, 3.00 \text{ M ClO}_4^-$$

The additions from the burettes were made in such a way that a selected value of h_s was attained; the preci-

Table 2. Survey of the experimental $-\log a (-\log A)_{B,h_s}$ data, given as $-\log a$ followed by $-\log A$ in parentheses.

$B = 0.001$ M, $\log h_s = -3.5$

5.7797 (3.9923)	5.4464 (3.6996)	5.1043 (3.4151)
4.8693 (3.2549)	4.6908 (3.1453)	4.6118 (3.1038)
4.4890 (3.0410)	4.4051 (3.0003)	4.2928 (2.9472)
4.1945 (2.9025)	4.1004 (2.8643)	3.9863 (2.8161)
3.8592 (2.7641)	3.7538 (2.7222)	3.6239 (2.6688)
3.5028 (2.6229)	3.3678 (2.5706)	3.2600 (2.5259)
3.1670 (2.4872)		

$B = 0.025$ M, $\log h_s = -3.6$

5.9009 (2.8524)	5.5840 (2.5596)	5.4001 (2.3912)
5.2245 (2.2350)	5.0778 (2.1120)	4.9376 (2.0005)
4.7953 (1.8948)	4.6462 (1.7936)	4.4966 (1.7056)
4.3390 (1.6237)	4.1538 (1.5413)	3.9687 (1.4692)
3.8000 (1.4111)	3.6325 (1.3581)	3.5223 (1.3248)
3.4446 (1.3022)		

$B = 0.075$ M, $\log h_s = -3.6$

5.7471 (2.3665)	5.4270 (2.0525)	5.2206 (1.8594)
5.0707 (1.7137)	4.9681 (1.6277)	4.8578 (1.5394)
4.7564 (1.4637)	4.6839 (1.4032)	4.6031 (1.3413)
4.5380 (1.2992)	4.4596 (1.2470)	

$B = 0.008$ M, $\log h_s = -3.9$

5.6927 (3.1752)	5.3690 (2.8835)	5.1842 (2.7162)
5.0438 (2.5996)	4.9391 (2.5107)	4.8117 (2.4143)
4.6951 (2.3288)	4.5781 (2.2527)	4.4648 (2.1842)
4.3492 (2.1223)	4.2339 (2.0660)	4.1151 (2.0142)
3.9711 (1.9581)	3.8372 (1.9097)	3.6993 (1.8618)
3.5754 (1.8273)	3.4550 (1.7922)	3.3418 (1.7610)
3.2370 (1.7319)	3.1263 (1.7018)	

$B = 0.025$ M, $\log h_s = -3.9$

5.8889 (2.9819)	5.5757 (2.6878)	5.3835 (2.5181)
5.1555 (2.3065)	5.0050 (2.1712)	4.8714 (2.0550)
4.7606 (1.9622)	4.6482 (1.8752)	4.5522 (1.8013)
4.4403 (1.7249)	4.3208 (1.6499)	4.1947 (1.5809)
4.0737 (1.5221)	3.9402 (1.4663)	3.7845 (1.4087)
3.6506 (1.3627)	3.5203 (1.3239)	3.4003 (1.2879)

$B = 0.001$ M, $\log h_s = -4.5$

5.7287 (4.2218)	5.4023 (3.9285)	5.2213 (3.7595)
5.0925 (3.6419)	4.9111 (3.4791)	4.7821 (3.3671)
4.6340 (3.2468)	4.4809 (3.1335)	4.3293 (3.0327)
4.1498 (2.9314)	3.9719 (2.8472)	3.8114 (2.7795)
3.6687 (2.7228)	3.5340 (2.6714)	3.4234 (2.6290)
3.3394 (2.5962)		

$B = 0.003$ M, $\log h_s = -4.5$

5.5973 (3.8041)	5.3212 (3.5200)	5.1121 (3.3094)
4.8900 (3.1035)	4.7576 (2.9809)	4.6565 (2.8896)
4.5588 (2.8017)	4.4626 (2.7202)	4.3697 (2.6460)
4.2791 (2.5790)	4.1787 (2.5120)	4.0669 (2.4462)
3.9290 (2.3780)	3.7856 (2.3175)	3.6269 (2.2629)
3.4376 (2.2045)	3.2556 (2.1510)	3.0925 (2.1030)

sion was ± 0.2 mV, as measured by the glass electrode. Seven titrations at four h_s levels were performed to give a total of 118 test solutions, at the following values of $-\log h_s(B)$: 3.50 (0.001); 3.60 (0.025 and 0.075); 3.90 (0.008 and 0.025); 4.50 (0.001 and 0.003). The experimental data in the form $-\log h(H)_B$ and
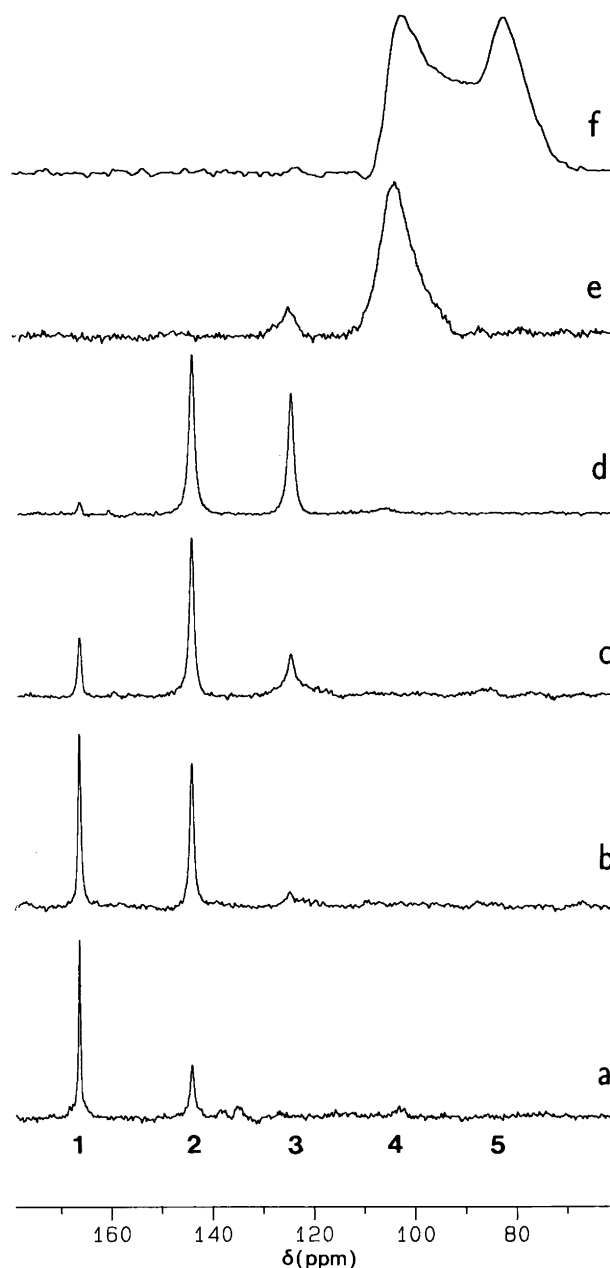

Fig. 1. 376.5 MHz ¹⁹F NMR spectra of aqueous solutions containing the following total concentrations (in mM) of U(VI) and fluoride: (a) 8.00, 4.00; (b) 8.00, 10.40; (c) 8.00, 14.50; (d) 8.00, 19.80; (e) 8.00, 91.20; (f) 8.00, 136.8. The number of fluoride ligands, n in $UO_2F_n^{2-n}$, is indicated by the numerals 1–5. The spectra have been recorded at a temperature of $-4°C$ at $-\log h = 4.30$. The ionic medium is 3.00 M NaClO₄. The spectra are base-line corrected and normalized so that the largest peak in each spectrum has the same height. The signal of the free fluoride (at about 0 ppm) present in spectra (c)–(f) is not shown.

Table 3. ^{19}F NMR shifts in ppm for the complexes $UO_2F_n^{2-n}$ in 3.00 M $NaClO_4$ solutions at $-\log h = 4.30$ and a temperature of $-4°C$. The shifts have been calculated against a 0.100 M NaF solution.^{a}

Species	δ(ppm)^a
F^-	0.00
UO_2F^+	165
UO_2F_2(aq)	143
$UO_2F_3^-$	123
$UO_2F_4^{2-}$	104.5
$UO_2F_5^{3-}$	≈ 83

^{a}The chemical shifts a of the various complexes varied a few tenths of a ppm, depending on the composition of the test solutions.

$-\log a(-\log A)_{B,h_s}$ are given in Tables 1 and 2, respectively.

Reagents, analysis and measurements. All experiments were made in a 3.00 M $NaClO_4$ ionic medium, at 25.00°C. The experimental data were obtained with a precision of 0.01 mV, using a computerised data aquisition system. All chemicals were of analytical grade and were analyzed using standard methods.

NMR data. ^{19}F NMR spectra have been recorded at 376.5 MHz, using a Bruker AM400 spectrometer. The NMR parameters were chosen so that quantitative spectra could be obtained: typically flip angle $\approx 30°(8 \; \mu s)$, pulse repetition time 6.4 s, spectral window 83 kHz

(covered by 32 k data points), number of scans 100–2000. The chemical shifts are reported in ppm towards higher frequency, with respect to an aqueous solution of 0.1 M NaF in 3 M $NaClO_4$ at 25°C. On this scale 0.1 M NaF in water, and neat CF_3COOH have chemical shifts at -1.1 and $+42.5$ ppm, respectively. A summary of the NMR data is given in Table 3 and Fig. 1.

Results and discussion

U(VI) hydrolysis in 3.00 M $NaClO_4$. The hydrolysis of U(VI) has been extensively studied; a recent review and critical evaluation has been published by Grenthe *et al.*[1] We have used the $E_g(H)_{B,A=0}$ data collected in the first part of each titration to test our experimental precision (and to obtain an independent check on the previous hydrolysis data). The experimental data used for this part are given in Table 1. A least-squares refinement of the data gave eqns. (3) and (4). The inclusion of additional

$$2\,UO_2^{2+} + 2\,H_2O \rightleftharpoons (UO_2)_2\,(OH)_2^{2+} + 2\,H^+,$$

$$\log \beta_{22} = -5.98 \pm 0.02 \qquad (3)$$

$$3\,UO_2^{2+} + 5\,H_2O \rightleftharpoons (UO_2)_3\,(OH)_5^+ + 3\,H^+,$$

$$\log \beta_{35} = -16.23 \pm 0.05 \qquad (4)$$
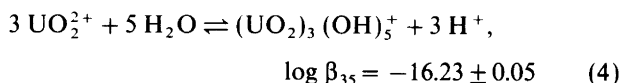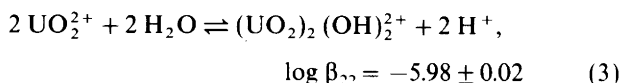
species into the chemical model did not improve the fit significantly.

These values are in good agreement with the values reported in Ref. 1, and those calculated from $\log \beta_{22}^0$ and
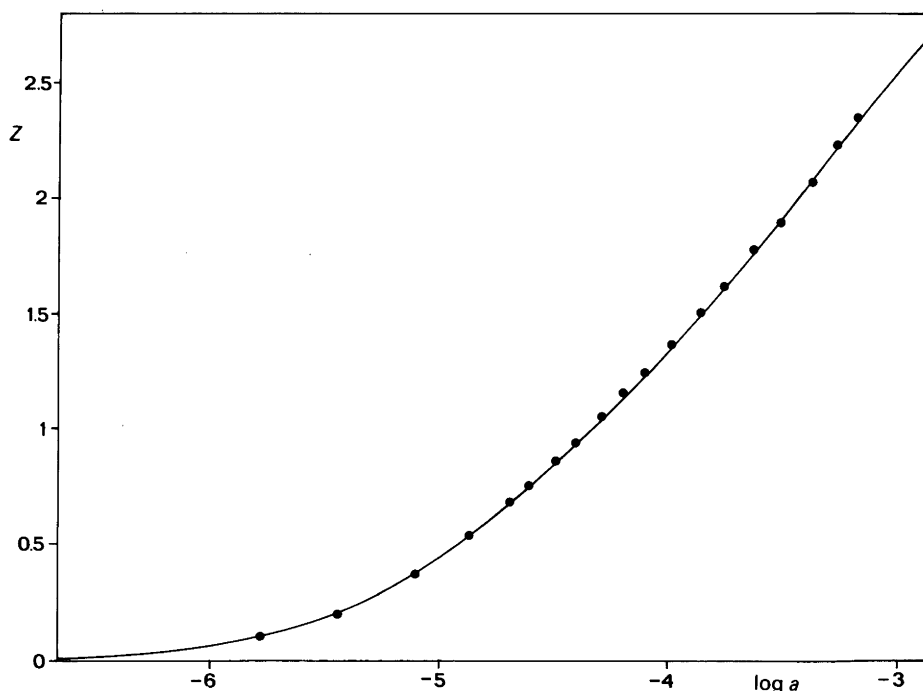

Fig. 2. The average number of coordinated fluoride per U(VI), Z, as a function of the free fluoride concentration, a. $Z = \{A - a(1 + Kh)\}/B$, where K is the protonation constant of F^-. The full-drawn curve has been calculated by assuming the formation of four complexes $UO_2F_n^{n-n}$, ($n = 1$–4).

Table 4. Equilibrium constants for the formation of $UO_2F_n^{2-n}$ complexes in 1.00 and 3.00 M $NaClO_4$ solutions, and estimated specific ion interaction coefficients deduced from these data.[a]

$\log \beta_n$ in 1.00 M $NaClO_4$	$\log \beta_n$ in 3.00 M $NaClO_4$	Specific ion interaction parameter ϵ $(n, ClO_4^-$ or $Na^+)/$kg mol^{-1}	ϵ estimated by Grenthe *et al.*[1]/kg mol^{-1}
4.54 ± 0.05	4.86 ± 0.02	0.28 ± 0.04	0.29 ± 0.05
7.98 ± 0.05	8.62 ± 0.04	0.13 ± 0.05^b	0.00
10.41 ± 0.05	11.71 ± 0.06	-0.14 ± 0.05	0.00 ± 0.05
11.89 ± 0.05	13.78 ± 0.08	-0.30 ± 0.06	-0.08 ± 0.06

[a]The experimental data are taken from Ahrland and Kullberg[15] and the present study. [b]In the simple specific ion interaction theory this interaction coefficient is expected to be zero.

$\log \beta_{35}^\circ$ and the corresponding ion interaction coefficients selected by Grenthe et al.,[1] $\log \beta_{22} = -5.93 \pm 0.08$ and $\log \beta_{35} = -16.28 \pm 0.27$, respectively.

The U(VI)–F⁻ system. The most precise study of the U(VI)–F⁻ system seems to be that of Ahrland and Kullberg,[15] who determined the stability constants of the binary complexes $UO_2F_n^{2-n}$, $n = 1–4$. Our experimental data from titrations made at $B = 0.001$ M and $\log h_s = -3.50$ [where the hydrolysis of U(VI) is negligible] were used to evaluate the stability constants for the binary UO_2^{2+}–F⁻ complexes. The following values were obtained: $\log \beta_1 = 4.86 \pm 0.02$, $\log \beta_2 = 8.62 \pm 0.04$, $\log \beta_3 = 11.71 \pm 0.06$ and $\log \beta_4 = 13.78 \pm 0.08$, respectively. A comparison between experimental data and this model is given in Fig. 2. The uncertainties are graphically estimated maximum errors.

The NMR data were obtained at much larger total concentrations of fluoride than those used in the EMF measurements. The fact that the various U(VI) fluoride complexes give separate NMR signals makes it easy to demonstrate directly the formation of $UO_2F_3^{-}$. (In the EMF method the concentration of the complexes is calculated from the difference between the total concentration of fluoride and the free [F⁻]; this difference is very uncertain when weak complexes are formed.) From the peak integrals it was possible to estimate an approximate value of $K_5 \approx 3$ M^{-1} for the equilibrium constant for reaction (5) at $-4°C$. The small value for the

$$UO_2F_4^{2-} + F^- \rightleftharpoons UO_2F_5^{3-} \tag{5}$$

equilibrium constant is probably the reason why the species $UO_2F_5^{3-}$ has not been detected previously. It is reasonable to assume that this species is the limiting complex and that it has the same pentagonal bipyramidal structure as that previously found in the solid state. The chemical shifts for the fluoride complexes are given in Table 3.
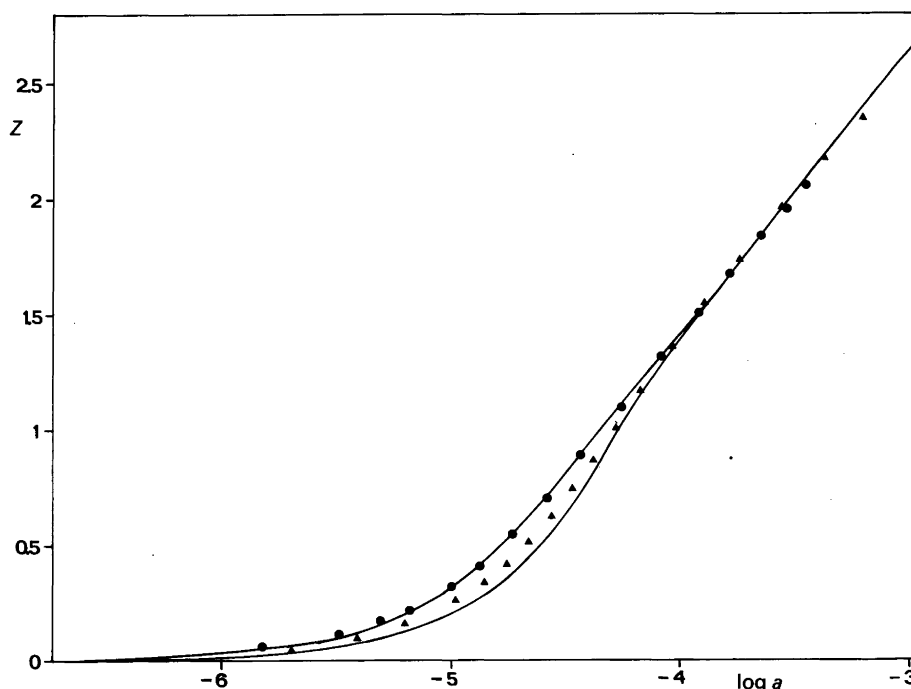

Fig. 3. Z as a function of the free fluoride concentration for titrations in the ternary system at $\log h_s = -4.50$. The symbols denote $B = 0.001$ M (●) and 0.003 M (▲).

There are no previous determinations of fluoride stability constants in 3 M $NaClO_4$: most of the previous experimental investigations have been made in solutions of unit ionic strength. From the equilibrium constants determined in this study, and from previous data from Ahrland and Kullberg,[15] the specific ion interaction coefficients, ε, for the various complexes have been calculated. The values obtained differ somewhat from the values *estimated* by Grenthe *et al.*,[1] c.f. Table 4. The interaction coefficient of the uncharged UO_2F_2 is equal to 0.13 ± 0.05. In the simple ion interaction theory this parameter is assumed to be zero. Both the interaction coefficients $\varepsilon(UO_2^{2+}, ClO_4^-) = 0.46$ kg mol^{-1} and $\varepsilon(Na^+, F^-) = 0.02$ kg mol^{-1} have been evaluated independently, c.f. Grenthe *et al.*[1]

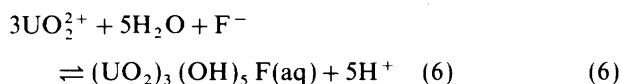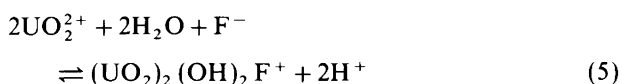*The ternary $UO_2^{2+}-OH^--F^-$ system.* The total concentration of U(VI) during the titrations at $-\log h_s = 3.6, 3.9$ and 4.5 is large enough for the formation of sizeable amounts of $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ in the absence of fluoride. The experimental data are given in Tables 1 and 2. A graphical analysis shows that Z is a function of the total concentration of U(VI), indicating the presence of polynuclear complexes. At larger concentrations of fluoride the curves merge, indicating that mononuclear species are formed. Analysis of the data at $-\log h_s = 3.6$ and 3.9 indicated that only the known binary U(VI)–hydroxide and fluoride complexes were formed. However, of the data at $-\log h_s = 4.5$ only those at the lowest value of B could be explained by this model: the data at $B = 0.003$ M deviate significantly, c.f. Fig. 3. The deviations observed cannot be explained by the formation of ternary complexes $(UO_2)_p(OH)_q F_r^{(2p-q-r)}$; if such complexes were formed the deviations would be expected to be in the opposite direction. The most reasonable explanation for the observed behaviour is the formation of small amounts of a precipitate. There is thus no evidence for the formation of ternary complexes in the concentration range available for experimental study. This conclusion is in agreement with the NMR measurements.

When fluoride is added to solutions containing polynuclear hydroxide complexes these are broken down, and mononuclear fluoride complexes are formed. All peaks observed in the ^{19}F NMR spectra are those assigned to the binary fluoride complexes, and there is no evidence for the formation of ternary species. The NMR data thus confirm the potentiometric investigations. The linewidths indicate that there is chemical exchange between the various fluoride complexes. The rate of exchange is faster for the higher complexes, and the rate increases with the total concentration of U(VI). At room temperature the signals are very broad and overlap, or even coalesce because of chemical exchange. Therefore, the spectra shown in Fig. 1 were recorded at $-4°C$, where the exchange is slower and the signals narrower.

The sensitivity of the ^{19}F NMR method and the large differences in chemical shifts between the various complexes offer an attractive possibility for the study of the rates and mechanisms of substitution reactions of UO_2^{2+}.

Estimation of upper limits for the equilibrium constants of possible ternary complexes. By using the known equilibrium constants for the various binary complexes and the known total concentrations of F^- and U(VI) it is possible to estimate a maximum value of the equilibrium constants for the ternary complexes $(UO_2)_2(OH)_2 F^+$ and $(UO_2)_3(OH)_5 F(aq)$, which might form by addition of one fluoride to the two predominant polynuclear complexes. The detection limit in the actual NMR spectra has been assumed to be 5% of the total concentration of fluoride. The calculation indicates that the equilibrium constants for the reactions (5) and (6) are $\log K_{221} \leqslant -2.2$

$$2UO_2^{2+} + 2H_2O + F^-$$
$$\rightleftharpoons (UO_2)_2(OH)_2 F^+ + 2H^+ \qquad (5)$$

$$3UO_2^{2+} + 5H_2O + F^-$$
$$\rightleftharpoons (UO_2)_3(OH)_5 F(aq) + 5H^+ \quad (6) \qquad (6)$$

and $\log K_{351} \leqslant -12.7$, respectively, indicating $\log K_1 \leqslant 3.8$, and $\log K_2 \leqslant 3.5$ for reactions (7) and (8), respectively.

$$(UO_2)_2(OH)_2^{2+} + F^- \rightleftharpoons (UO_2)_2(OH)_2 F^+ \qquad (7)$$

$$(UO_2)_3(OH)_5^{2+} + F^- \rightleftharpoons (UO_2)_3(OH)_5 F(aq) \qquad (8)$$

The maximum values of these constants are about a factor of ten smaller than the equilibrium constant for the formation of UO_2F^+, i.e., the same change as previously found for the corresponding $Be(II)-OH^--F^-$ system.

A spectrophotometric study of the spectra of the test solutions did not indicate the presence of significant amounts of ternary complexes. It would be feasible to detect the formation of ternary complexes at higher total concentrations of U(VI). However, the precipitation of $UO_2(OH)_2$ (s) prevents such a study.

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