Formation Constants of $\text{HF}_m^{(1-m)+}$ and $\text{UO}_2\text{F}_n^{(2-n)+}$ Complexes in 1 mol dm^{-3} (NaCl) Medium

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1 Introduction

Extensive studies have been carried out for the complex formation between uranyl and fluoride ions in solution^{1). Among them, the work by Ahrlund and his coworkers^{2)~4)} may be emphasized, in which they determined the formation constants and other thermodynamic quantities in a 1 mol dm^{-3} sodium perchlorate solution.}

Knowledge of the complex formation of uranyl and fluoride ions in a chloride medium than in a perchlorate medium may be more useful for practical purposes in connection with problems of atomic fuels. Collection of uranyl ions from sea water may be another interest in the chloride medium. However, very few formation constants have been determined for fluoro complexes of uranyl ions in chloride media in which the formation constants of hydrogen fluoride complexes have been determined under the same experimental conditions. Therefore, the aim of the present work is to add to the literature the reliable values of the formation constants of fluoro complexes of uranyl ions in a chloride medium.

2 Experimental

2.1 Reagents

Uranyl chloride was prepared by the method described previously^{5). The concentration of uranyl ions in the stock solution was gravimetrically determined in the form of U_3O_8 . Other chemicals used were of reagent grade.}

2.2 Apparatus

All solutions containing fluoride ions were stored in polyethylene bottles. The titration cell was coated with paraffin. A fluoride-ion selective electrode (Orion 94-09 electrode) was used for determination of the concentration of free fluoride ions. An integrating digital voltmeter (Takeda Riken TR-6011) was employed to measure emf's of the fluoride-ion selective electrode against an Ag-AgCl electrode as a reference. Constant and reproducible emf's were obtained within a minute. The uncertainty of the emf's was within ± 0.01 mV at each point of measurements.

2.3 Method of measurement

All the measurements were performed at $25.00 \pm 0.01^\circ\text{C}$ in a paraffin oil bath. The ionic medium was kept constant at 1 mol dm^{-3} (NaCl), so that the activity coefficient of fluoride ions, as well as those of other reacting species, was assumed to be constant. Since the liquid junction potential at the interface between the test solution and the salt bridge connected with the reference half-cell was negligible under the present experimental conditions, the emf (in mV) of the cell is represented at 25°C as follows :

$$E = E^\circ - 59.15 \log [\text{F}^-] \quad (1)$$

where E° is a constant and was determined by means of a Gran plot⁶⁾ at the beginning of each titration of the test solutions in which no uranyl ion was present and pH ($= -\log [\text{H}^+]$) was so high that the association of fluoride ions with hydrogen ions was negligible. Then a desired amount of the stock solution of uranyl chloride was added to the test solution. An aliquot of a hydrochloric acid solution was also added to the test solution in order to keep the concentration of hydrogen ions at approximately 0.1

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mol dm⁻³ and to prevent the hydrolysis of uranyl ions. The total concentration of uranyl ions was kept constant throughout a titration.

3 Results and Discussion

3.1 Complex formation between proton and fluoride ions

The titration curves were well explained in terms of the formation of the HF and HF₂⁻ complexes, as have been reported by many authors¹⁾. The formation constants β_{11} ($=[\text{HF}]/[\text{H}^+][\text{F}^-]$) and β_{12} ($=[\text{HF}_2^-]/[\text{H}^+][\text{F}^-]^2$) were obtained by analyzing the formation function $\bar{n}_{\text{F(H)}}$, which is given as follows:

$$\bar{n}_{\text{F(H)}} = \frac{[\text{HF}] + 2[\text{HF}_2^-]}{[\text{H}^+] + [\text{HF}] + [\text{HF}_2^-]} = \frac{\beta_{11}[\text{F}^-] + 2\beta_{12}[\text{F}^-]^2}{1 + \beta_{11}[\text{F}^-] + \beta_{12}[\text{F}^-]^2} = \frac{C_{\text{F}} - [\text{F}^-]}{C_{\text{H}}} \quad (2)$$

where C_{F} and C_{H} denote the total concentrations of fluoride and (dissociable) hydrogen ions, respectively. The maximum value of $\bar{n}_{\text{F(H)}}$ obtained in this measurement was 1.2. The formation constants were calculated with a least-squares method by minimizing the error square sum, $U = \sum (1 - \bar{n}_{\text{F(H) calc}} / \bar{n}_{\text{F(H)}})^2$, where $\bar{n}_{\text{F(H) calc}}$ represents the calculated value of $\bar{n}_{\text{F(H)}}$ by using a particular set of β_{11} and β_{12} . The results were tabulated in Table 1.

3.2 Complex formation between uranyl and fluoride ions

From titration curves obtained at different concentrations of uranyl ions, we calculated the formation function $\bar{n}_{\text{F(M)}}$ as follows:

$$\bar{n}_{\text{F(M)}} = \frac{\sum p[(\text{UO}_2)_q \text{F}_p^{(2q-p)+}]}{[\text{UO}_2^{2+}] + \sum q[(\text{UO}_2)_q \text{F}_p^{(2q-p)+}]} = \frac{C_{\text{F}} - [\text{F}^-] - [\text{HF}] - 2[\text{HF}_2^-]}{C_{\text{M}}} = \frac{C_{\text{F}} - [\text{F}^-] - \beta_{11}[\text{H}^+][\text{F}^-] - 2\beta_{12}[\text{H}^+][\text{F}^-]^2}{C_{\text{M}}} \quad (3)$$

Table 1 Formation constants of hydrogen fluoride complexes

Reference	Medium	Temperature	log β_{11}	log β_{12}
This work	1.0 mol dm ⁻³ NaCl	25.0°C	2.84 ± 0.01	3.34 ± 0.03
Ref. 7	1.0 mol dm ⁻³ NaCl	25.0°C	2.887 ± 0.009	3.87 ± 0.01
Ref. 4	1.0 mol dm ⁻³ NaClO ₄	20.0°C	2.93 ± 0.01	3.42 ± 0.05
Ref. 2	1.0 mol dm ⁻³ NaClO ₄	25.0°C	2.95 ± 0.01	3.53 ± 0.11
Ref. 8	1.0 mol dm ⁻³ NaClO ₄	25.0°C	2.95 ± 0.01	3.48 ± 0.02
Ref. 9	1.0 mol dm ⁻³ NaNO ₃	25.0°C	2.90 ± 0.03	3.67 ± 0.08

Uncertainties of the formation constants were estimated as 3σ where σ denotes the standard deviation.

where C_{M} denotes the total concentration of uranyl ions in the solution. The concentration of hydrogen ion was given as follows:

$$[\text{H}^+] = C_{\text{H}} / (1 + \beta_{11}[\text{F}^-] + \beta_{12}[\text{F}^-]^2) \quad (4)$$

when no hydrolysis of uranyl ion occurs. Since the formation curve obtained was independent of the total uranyl concentration (see Fig. 1), it was obvious that only mononuclear complexes were formed ($q=1$ in eq. 3). Since the maximum value of $\bar{n}_{\text{F(M)}}$ was 3.5, a series of $\text{UO}_2\text{F}_n^{(2-n)+}$ complexes with $n=1-4$ seems to be present. A least-squares calculation for obtaining the best values of β_n ($=[\text{UO}_2\text{F}_n^{(2-n)+}]/[\text{UO}_2^{2+}][\text{F}^-]^n$) was carried out to minimize the

Fig. 1 The average number of fluoride ions bound per uranyl ion, $\bar{n}_{\text{F(M)}}$, as a function of $-\log [\text{F}^-]$

The solid line shows a calculated curve using the constants in Table 2

Table 2 The formation constants of uranyl fluoride complexes

Reference	Medium	Temp.	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
This work	1.0 mol dm ⁻³ NaCl	25.0°C	4.39±0.02	7.77±0.02	9.83±0.03	10.81±0.10
Ref. 2	1.0 mol dm ⁻³ NaClO ₄	25.0°C	4.54±0.01	7.98±0.01	10.42±0.02	11.9 ±0.03
Ref. 4	1.0 mol dm ⁻³ NaClO ₄	20.0°C	4.54±0.05	7.89±0.05	10.46±0.06	11.8 ±0.11

Uncertainties of the formation constants were estimated as 3σ where σ denotes the standard deviation.

error square sum with respect to $\bar{n}_{\text{F(M)}}$. The final results were listed in Table 2, together with values reported by previous authors in 1 mol dm⁻³ ionic media. The difference between values in the sodium chloride and sodium perchlorate media might be attributed to the formation of chloro complexes of uranyl ions in the former system.

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