^{19}F Nuclear Magnetic Resonance Study on the Kinetics of the Fluoride Exchange in Uranium(VI) Fluoro Complex

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Kinetics of the fluoride exchange in uranium(VI) (uranyl) fluoro complex was studied by using ^{19}F NMR. The ^{19}F NMR signal of coordinated fluoride at the equatorial positions of uranyl ion was first observed at about 80 ppm down field from that of bulk F$^-$. From area measurements of the coordinated and free ^{19}F NMR signals, pentafluoro complex $UO_2F_5^{3-}$ was confirmed to exist in aqueous solutions containing high concentration of fluoride ion. The stability constant $K_5=[UO_2F_5^{3-}]/[UO_2F_4^{2-}][F^-]$ was determined to be 1.31 mol^{-1} kg. The rate of F$^-$ exchange between coordinated and bulk F$^-$ was measured by the ^{19}F NMR line-broadening method and the observed first-order rate constant k_{obsd} was expressed as $k_{obsd}=(k_4+k_5K_5[F^-])[F^-]/(1+k_5[F^-])$ where k_4 and k_5 are the exchange rate constants of F$^-$ between bulk and coordinated F$^-$ in $UO_2F_4^{2-}$ and $UO_2F_5^{3-}$, respectively. The associative or associative interchange mechanism was proposed from the experimental results.

Kinetics of ligand exchange and substitution reactions of uranyl complexes have been studied extensively.[1-16] Of these studies a method using nuclear magnetic resonance is of major importance. In spite of many NMR studies, no paper has been reported on the fluoride exchange in uranyl fluoro complex. One of the main reason is that the complexation between uranyl and fluoride ions has not been yet established in high concentrations of fluoride ion, and hence the accurate exchange rate constant can not be determined by the ^{19}F NMR method. Ahrland and Kullberg,[17] and Ishiguro et al.[18] reported the stability constants of uranyl fluoro complexes. In both studies, the maximum coordination number was four, i.e. the highest complexation was $UO_2F_4^{2-}$. However, it has been known that the coordination number of uranyl complexes is generally five in the equatorial plane, with only few exceptions of six-coordinate e.g., $UO_2(CO_3)_3^{4-}$ [19] and four-coordinate e.g. $UO_2(HMPT)_4^{2+}$ (HMPT=hexamethylphosphoramide).[5] Indeed, a pentagonal bipyramidal structure of $UO_2F_5^{3-}$ was reported in a crystal X-ray study.[20] In view of these earlier studies, a question arises whether five-coordinate $UO_2F_5^{3-}$ exists or not in aqueous solutions. In the present study, we observed the ^{19}F NMR signal of coordinated F$^-$ at the equatorial positions of uranyl ion and confirmed the existence of $UO_2F_5^{3-}$ by the area measurements of NMR signals. This paper presents the results of the equilibrium between uranyl and fluoride, and the kinetics of fluoride exchange in uranyl fluoro complexes by using ^{19}F NMR.

Experimental

All chemicals used were reagent grade. Uranyl stock solution was prepared by dissolving uranyl nitrate into deionized water. The concentration of uranyl solution was determined by colorimetry. Sodium fluoride and potassium fluoride were preliminary dried in a vacuum drier at 80 °C for one day, and then weighed and dissolved in deionized water. In equilibrium experiments, the total concentration of sodium fluoride and sodium perchlorate was adjusted to be 1.0 mol kg^{-1}, and the total concentration of UO_2^{2+} was kept constant at 0.05 mol kg^{-1}. In kinetic experiments, potassium fluoride was used in order to gain high solubility of F$^-$ and the ionic strength was not adjusted. The pH of solutions was measured with a Hitachi-Horiba Model F-7s pH meter. A JEOL JNM-FX 100 NMR spectrometer equipped with a NM-PVTS1 temperature controller was used for the NMR measurements. NMR measurements were also carried out under the irradiation of laser by a laser irradiation NMR instrument, which was developed in our laboratory to measure high resolution NMR spectra under the continuous laser irradiation using an argon ion laser (Spectra Physics 2025-05S). A Shimadzu UV-365 spectrophotometer was used for measurements of UV-visible absorption spectra.

Results and Discussion

^{19}F NMR Spectra. ^{19}F NMR spectra of aqueous fluoride ion exhibit remarkable broadening at pH<7 due to the exchange between F$^-$ and HF. Therefore, pH of solutions was kept at about 7.6 by adding perchloric acid in all experiments in order to avoid the broadening due to the above interaction. The hydrolysis of uranyl ion was not observed under the above conditions by UV-visible absorption spectrum and ^{19}F NMR measurements. Figure 1 shows ^{19}F NMR spectra of the solutions containing 0.5 mol kg^{-1} of F$^-$ and various concentrations of UO_2^{2+}. As shown in Fig. 1, distinct two peaks are observed. The signal in the lower field becomes smaller as the concentration of UO_2^{2+} decreases and finally disappears in the absence of UO_2^{2+}. Therefore, this signal in the lower field can be assigned as that of coordinated F$^-$ at the equatorial positions of UO_2^{2+}, while the signal in the higher field as bulk F$^-$. A remarkable change in the chemical shift of the coordinate F$^-$ signal with changing uranyl concentrations might be attributed to the chemical exchange with free F$^-$ as will be described later. The area ratio of these NMR signals gives the concentration ratio of F$^-$ between coordinated and free sites. Therefore, the number of coordinated fluoride and the stability constant can be determined, if the total

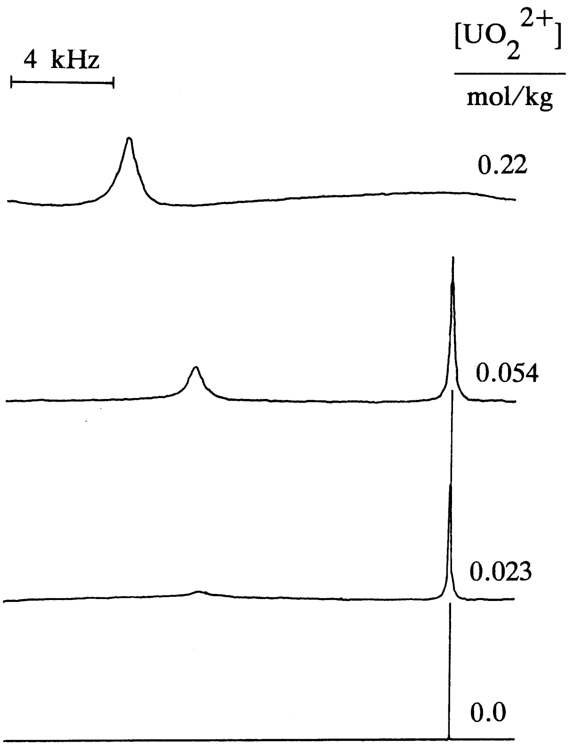

Fig. 1. ^{19}F NMR spectra of solutions containing 0.5 mol kg^{-1} of NaF at various uranyl concentrations.

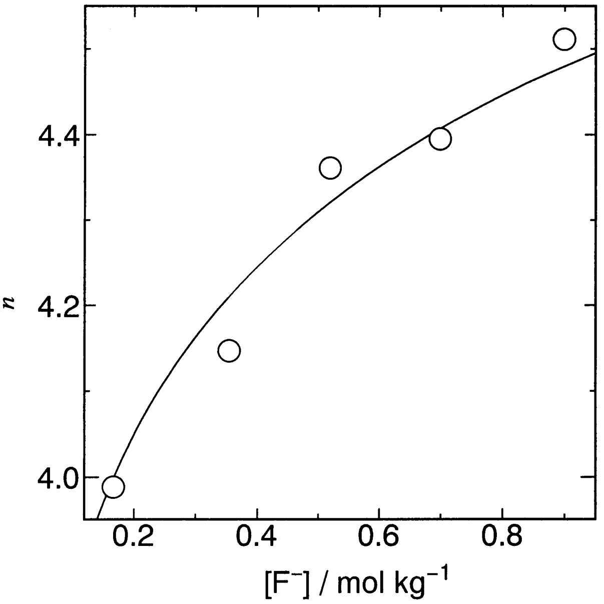

Fig. 2. Plot of $\bar{n}$ against [F$^-$] at 0 °C. $[UO_2^{2+}]_T=0.05$ mol kg^{-1}. The solid line denotes the non-linear least-square best-fit line.

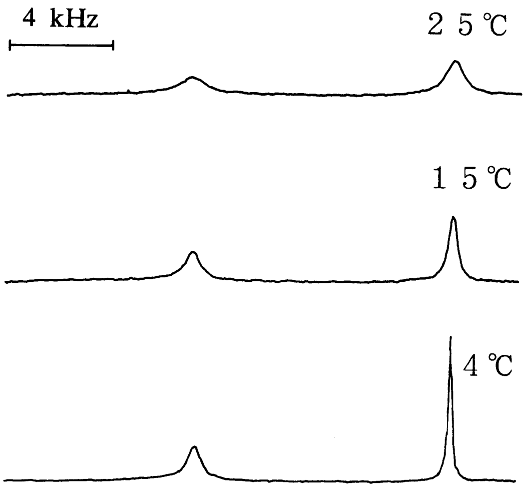

Fig. 3. ^{19}F NMR spectra of the solution containing 0.5 mol kg^{-1} of NaF and 0.0054 mol kg^{-1} of total uranyl concentration at various temperature.

concentrations of uranyl and fluoride ions are known.

The average coordination number $\bar{n}$ is defined as

$$\bar{n} = [F^-]_{coord}/[UO_2^{2+}]_T,$$

where $[F^-]_{coord}$ refers to the concentration of coordinated F^- and $[UO_2^{2+}]_T$ denotes total concentration of UO_2^{2+}. In Fig. 2, $\bar{n}$ is plotted as a function of the concentration of free fluoride [F$^-$], i.e. $[F^-]=[F^-]_T-[F^-]_{coord}$. As seen in Fig. 2, $\bar{n}$ tends to exceed 4 in high [F$^-$]. This clearly indicates that the species $UO_2F_5^{3-}$ exists in such solutions. Since UO_2F_2 and the lower fluoro species are neglected under the present conditions,[17] $\bar{n}$ can be written by,

$$\bar{n} = (3[UO_2F_3^-] + 4[UO_2F_4^{2-}] + 5[UO_2F_5^{3-}])/[UO_2^{2+}]_T,$$

where $[UO_2F_n^{2-n}]$ denotes the concentration of these complexes. Since K_4 is known to be 30.9 mol^{-1} dm^3 by Ahrland, $\bar{n}$ is simply related to $[UO_2F_5^{3-}]$ yielding the stability constant K_5, i.e. $K_5=[UO_2F_5^{3-}]/[UO_2F_4^{2-}][F^-]$. In Fig. 2, a non-linear least square's fit of the above equation agrees well with the experimental values and the value of K_5 can be determined to be 1.31 mol^{-1} kg. According to Ahrland, K_4 is smaller at about one order than K_3. This is consistent with the present result, because K_5 is also smaller at the one order than K_4. The reason that $[UO_2F_5^{3-}]$ was only observed in the present study was that in the earlier potentiometric studies[17,18] experiments were carried out in such low fluoride solution ([F$^-$]<0.1 mol dm^{-3}) that the concentration of $UO_2F_5^{3-}$ was too low to be observed.

F$^-$ Exchange Reaction. In Fig. 3, ^{19}F NMR signals of both coordinated and free F$^-$ become broader with increasing temperature. This indicates that the exchange takes place between coordinated and free F$^-$ as follows:

$$UO_2F_n^{(n-2)-} + {}^*F^- \rightleftharpoons UO_2F_{(n-1)}{}^*F^{(n-2)-} + F^-, \qquad (1)$$

where the asterisk denotes a substituting ligand. The reason that the coordinated F$^-$ signal shifts to the lower field with increasing temperature could be attributed to the paramagnetic contribution of the uranyl ion. Similar behavior was observed in the ^{17}O NMR signal of uranyl oxygens, i.e. the ^{17}O NMR signal of uranyl oxygens shifts toward the lower field as temperature increases because the paramagnetic contribution increases with temperature.[21] Thus, the chemical shift of the coordinated F^- signal is affected by the paramagnetic interaction as well as the chemical exchange. Therefore, we determined the rate of exchange for reaction (1) by measuring the relaxation time of the free F^- signal.

The life time of fluoride ions staying in the first coordination sphere of uranyl ion, τ_m, is related to the well known Eq. 2,[22]

$$1/T_2 - 1/T_{2a} = p_m/\tau_m, \quad (2)$$

where T_2 and T_{2a} are the transverse relaxation times in the presence and the absence of uranyl complex, respectively, and p_m is defined under conditions $[F^-]_T \gg [UO_2^{2+}]_T$ as

$$p_m = n[UO_2^{2+}]_T/[F^-]_T. \quad (3)$$

The first order rate constant k_{obsd} for Eq. 1 is related to τ_m as $k_{obsd}=1/\tau_m$. In Fig. 4, $\log(1/T_2-1/T_{2a})$ is plotted against the reciprocal temperature, $1/T$. The plot in Fig. 4 is linear with a negative slope over the temperature region studied. This indicates that the line-broadening is controlled by the chemical exchange and that Eq. 2 can be applicable for determining the exchange rate. The value of k_{obsd} was determined from Eqs. 2 and 3, by using K_5=1.31 mol^{-1} kg. In Fig. 5, k_{obsd} is plotted as a function of $[F^-]$. The plot shows curvature, but k_{obsd} increases continuously with $[F^-]$. This behavior differs from a saturated function generally observed for reactions involving pre-equilibriums.

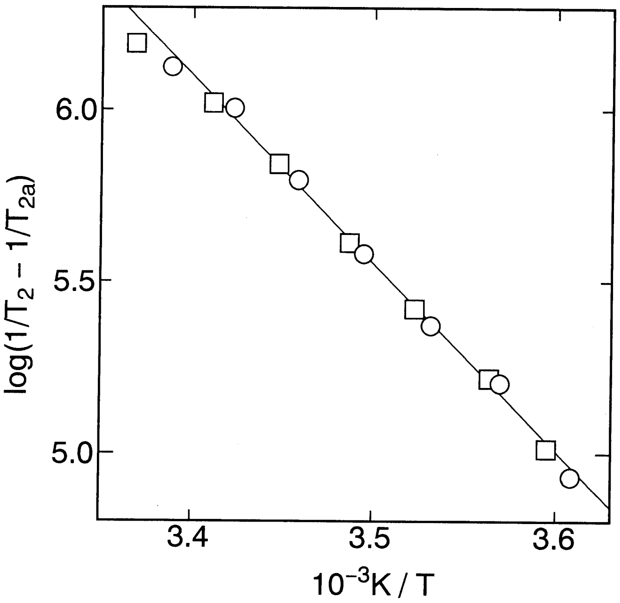

Fig. 4. Plots of log $(1/T_2-1/T_{2a})$ against $1/T$. $[UO_2^{2+}]$= 0.0366 mol kg^{-1}; $[F^-]$=0.50 mol kg^{-1}. (○): no irradiation, (□): irradiation at 488 nm, 1 W.

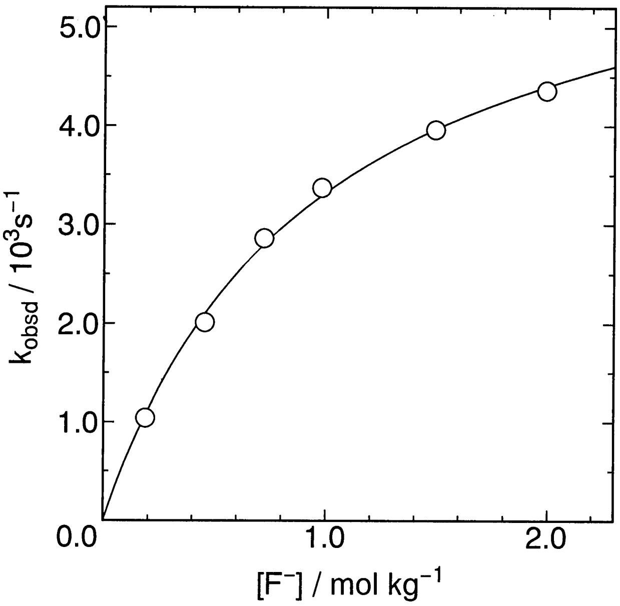

Fig. 5. Plot of the first-order rate constant k_{obsd} against $[F^-]$ for the exchange of F^- in uranyl fluoro complex at 25 °C. The solid line denotes the non-linear least-square best-fit line.

Under the present kinetic conditions, the main uranyl species are $UO_2F_4^{2-}$ and $UO_2F_5^{3-}$. It would be no doubt that the structure of $UO_2F_5^{3-}$ takes a pentagonal bipyramidal structure, where five fluorie ions occupy the equatorial position. This pentagonal bipyramidal structure is common in most of uranyl complexes. For example, even in large bis(acetylacetonato)uranyl complex, solvent such as dimethyl sulfoxide coordinates to the equatorial position, forming the pentagonal bipyramidal structure $UO_2(acac)_2dmso$.[14] Considering these facts, the structure of $UO_2F_4^{2-}$ is most likely to be the same as that of $UO_2F_5^{3-}$, one water molecule taking in the equatorial position. Therefore, tetra-fluoro complex should be written as $UO_2F_4(H_2O)^{2-}$ (for purpose of simplicity we will write this complex as $UO_2F_4^{2-}$).

Based on the assumption that both tetra- and penta-fluoro complexes take the same pentagonal bipyramidal structure, the exchange reaction of F^- would be expressed by the following two independent paths with $UO_2F_4^{2-}$ and $UO_2F_5^{3-}$.

$$UO_2F_4^{2-} + {}^*F^- \rightleftharpoons UO_2F_3{}^*F^{2-} + F^-, \quad (4)$$

$$UO_2F_5^{3-} + {}^*F^- \rightleftharpoons UO_2F_4{}^*F^{3-} + F^-. \quad (5)$$

If the above reactions are assumed to be first order in both complexes and F^-, the over-all rate can be expressed by

$$\text{Rate} = k_4[\text{UO}_2\text{F}_4{}^{2-}][\text{F}^-] + k_5[\text{UO}_2\text{F}_5{}^{3-}][\text{F}^-], \qquad (6)$$

where k_4 and k_5 are the rate constants in Eqs. 4 and 5, respectively. By replacing $[\text{UO}_2\text{F}_4{}^{2-}]$ and $[\text{UO}_2\text{F}_5{}^{3-}]$ by $[\text{UO}_2]_\text{T}$ using K_5=$[\text{UO}_2\text{F}_5{}^{3-}]/[\text{UO}_2\text{F}_4{}^{2-}][\text{F}^-]$ and $[\text{UO}_2]_\text{T}$= $[\text{UO}_2\text{F}_4{}^{2-}]$+$[\text{UO}_2\text{F}_5{}^{3-}]$, Eq. 6 yields

$$\begin{aligned}\text{Rate} &= [\text{UO}_2]_\text{T}(k_4 + k_5K_5[\text{F}^-])[\text{F}^-]/(1 + K_5[\text{F}^-]) \\ &= k_\text{obsd}[\text{UO}_2]_\text{T}, \qquad (6')\end{aligned}$$

and the observed rate constant k_obsd can be expressed by

$$k_\text{obsd} = (k_4 + k_5K_5[\text{F}^-])[\text{F}^-]/(1 + K_5[\text{F}^-]). \qquad (7)$$

In Fig. 5, a solid line shows a non-linear least square's fit to Eq. 7. The calculated line agrees well with experimental values, giving the values of k_4 and k_5 to be 6.96×10^3 and 4.34×10^1 mol^{-1} dm^3 s^{-1}, respectively. The calculation also deduces the K_5 value to be 1.1 mol^{-1} kg, which is in good agreement with the value determined by the NMR area measurements.

From Fig. 4, the activation enthalpy and entropy were determined to be 39.9 ± 0.8 kJ mol^{-1} and -128 ± 3 J K^{-1} mol^{-1}, respectively for the apparent second order tate constant defined as $k_\text{obsd}/[\text{F}^-]$. Under the conditions of Fig. 4, the apparent second order rate constant mainly reflects k_4 path, considering that k_4 is much larger than k_5, e.g. k_4/k_5=160, although $[\text{UO}_2\text{F}_4{}^{2-}]$ is comparable with $[\text{UO}_2\text{F}_5{}^{3-}]$. The large negative value of activation entropy suggests the associative nature of the reaction mechanism. It was found that k_5 was much smaller than k_4. This can be also explained in terms of the associative or associative interchange mechanism, bacause the electrostatic repulsion should be larger for the associative interaction between $\text{UO}_2\text{F}_5{}^{3-}$ and F^- compared with the corresponding interaction between $\text{UO}_2\text{F}_4{}^{2-}$ and F^-. It would be also unfavorable for k_5 path, because the additional complex formation to $\text{UO}_2\text{F}_5{}^{3-}$ is expected to be more unstable compared with that to $\text{UO}_2\text{F}_4{}^{2-}$.

On the other hand, if the structure of $\text{UO}_2\text{F}_4{}^{2-}$ is assumed to be tetragonal-bipyramidal, the following exchange should be taken into account.

$$\text{UO}_2\text{F}_4{}^{2-} + \text{F}^- \rightleftharpoons \text{UO}_2\text{F}_5{}^{3-}. \qquad (8)$$

In this exchange, the magnetic property of bulk F^- is only sensible in the reverse process, while the forward one affects only the signal of coordinated F^-. Since k_obsd is related to the relaxation time of bulk F^- signal, k_obsd is expected to be independent of $[\text{F}^-]$ by the above exchange. As seen in Fig. 5, k_obsd is extrapolated to the origin within experimental errors and hence the contribution of the exchange by Eq. 8 can be ruled out.

The associative nature is supported by the result of laser irradiation NMR experiments. It can be seen in Fig. 3 that the exchange rate is not affected by the irradiation of 1.0 W argon ion laser at 488 nm. In an earlier study, the intra-molecular ligand exchange reaction in $\text{UO}_2(\text{acac})_2$dmso was accelerated by the same laser irradiation, because the laser irradiation weakened the bond between uranyl and dmso resulting in the acceleration of the dissociative exchange reaction in the excited state.[23] However, in an associative reaction, a photo-excited state would not necessarily be favorable to form an intermediate with an additional ligand and hence would not accelerate the reaction rate.

In the kinetic experiments, ionic strength was not adjusted, because of the poor solubility of NaF in the presence of NaClO_4. Therefore, in order to see the difference of k_obsd at different ionic strengths, k_obsd was determined in solutions containing 0.5 and 1.0 mol kg^{-1} of NaClO_4, otherwise the condition being kept constant. It was found that k_obsd was larger about 3% in 1.0 than 0.5 mol kg^{-1} NaClO_4 solution. The change in k_obsd with ionic strength, which is almost within errors of the NMR line-shape analysis, is too small to be attributed to the electrostatic interaction. This suggests that the dependence of k_obsd, and hence the calculated values of k_4 and k_5, on ionic strength is small and would be about 10% at most under the present experimental conditions.

In ligand exchange reactions in uranyl complexes, such as dimethyl sulfoxide complex, the dissociative or interchange mechanism was proposed.[13] As compared with bulky organic ligands, the samll size of fluoride ion and its strong affinity towards uranyl ion would be responsible for the associative nature of the fluoride exchange.

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