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Study of Complex Formation of Dioxouranium(Ⅵ) Ion with Nitrate Ion by ^{17}O NMR Spectroscopy

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산소-17 핵자기공명분광법을 이용한 디옥소우라늄(Ⅵ) 이온의 질산 이온과의 착물형성에 관한 연구

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Abstract: The interaction of dioxouranium(Ⅵ) (uranyl) ion with nitrate ion has been studied by ^{17}O NMR spectroscopy. The ^{17}O resonance of uranyl oxygen atoms(uranyl oxygens hereafter) of $UO_2NO_3^+$ was at lower field than that of uranyl ion. The stability constants of $UO_2NO_3^+$ were obtained from the variation of ^{17}O chemical shifts with nitrate-ion concentration at 5, 15, 25, 35℃ and depend on the ionic strength. Thermodynamic parameters calculated from temperature dependence of the stability constants were as follows: $\Delta H = -(27.2 \pm 1.7)$ kJ mol^{-1} and $\Delta S = -(110 \pm 7)$ JK^{-1}mol^{-1}. There was a linear relationship between the enthalpy and entropy for 1:1 complex formation of the uranyl ion with a variety of anionic ligands.

요 약: 디옥소우라늄(Ⅵ) (우라닐) 이온과 질산 이온과의 상호작용을 산소-17 핵자기공명분광법으로 연구하였다. $UO_2NO_3^+$의 우라닐 산소 원자(이후 우라닐 산소)의 산소-17 공명신호는 우라닐 이온의 그것보다 낮은 자기장에서 나타났다. $UO_2NO_3^+$의 안정도상수를 5, 15, 25, 35℃에서 질산 이온 농도에 따른 산소-17 화학적 이동의 변화로부터 구했으며, 그 값은 이온강도에 따라 달랐다. 안정도상수의 온도 의존성으로부터 계산한 열역학적 파라미터는 다음과 같다: $\Delta H = -(27.2 \pm 1.7)$kJ mol^{-1}와 $\Delta S = -(110 \pm 7)$JK^{-1}mol^{-1}. 우라닐 이온과 여러가지 음이온의 배위자와의 1:1 착물형성 반응에 대한 엔탈피와 엔트로피 사이에는 직선관계가 있었다.

1. INTRODUCTION

Oxygen-17 nuclear magnetic resonance (NMR) spectroscopy is of special significance for physical and coordination chemistry owing to the great number of oxygen-containing compounds and solvents[1]. The ^{17}O nucleus is, however, a difficult nucleus to observe by NMR spectroscopy[2, 3]. First, the nucleus is a spin 5/2 nucleus with an appreciable electric quadrupole moment($Q = -2.6 \times 10^{-30}$m^2) which in general leads to rapid nuclear quadrupole

relaxation. Second, ^{17}O NMR is problematic due to the low natural abundance of ^{17}O(0.037 %), which usually necessitates the use of samples enriched by an expensive ^{17}O isotope. Recently many of the difficulties experienced in ^{17}O NMR have been removed by the advent of Fourier transform techniques and convenient method for ^{17}O enrichment from readily available sources. ^{17}O NMR spectroscopy is very useful in studying the chemistry of uranyl ion because ^{17}O chemical shifts of uranyl oxygens are very sensitive to the equatorial ligands[4] and their ^{17}O relaxation time is very long(T_1= 0.24 s at 25℃:[5] their ^{17}O resonance is, in fact, the sharpest of ^{17}O resonances known).

Recently much studies on chemical behaviors of actinoid elements have been carried out in order to provide answers on the fate of these elements in potential nuclear waste disposal sites and in the environment. Stability constants for complex formation of the uranyl ion with anionic ligands(such as nitrate, chloride, fluoride, and sulfate ions) are fundamental and important in understanding chemical behaviors of the uranyl ion in aqueous solution. The interaction of the uranyl ion with nitrate ion has been investigated by spectrophotometric[6, 7], electrochemical[8, 9], and distribution methods[10] and known to be relatively weak in aqueous solution. The purpose of the present work is to study the interaction of the uranyl ion with nitrate ion by ^{17}O NMR spectroscopy and to compare the results obtained by this method with those found by other techniques. The thermodynamic parameters calculated from stability constants at different temperatures are given and compared with those on complex formation of the uranyl ion with other anionic ligands.

2. EXPERIMENTAL

The uranyl complex used was pentaaquadioxouranium(Ⅵ) perchlorate $[UO_2(H_2O)_5](ClO_4)_2$, which was prepared by dissolving $UO_3 \cdot 2H_2O$ in 60% perchloric acid (Wako Pure Chemical Ind., Ltd). The $UO_3 \cdot 2H_2O$ was prepared by using the method of Ekstrom et al [11]. The uranyl complex was recrystallized from distilled water five times, and the resulting crystals were dried *in vacuo*. Sodium perchlorate (Wako) and sodium nitrate (Wako) were recrystallized twice from aqueous solution before use. The concentrations of uranyl and hydrogen ions in all sample solutions were 0.11 and 0.08m(1m=1mol/kg), respectively. The ionic strengh of 5.0 m was adjusted by using sodium perchlorate.

The procedure for preparation of ^{17}O-enriched uranyl oxygens is described in the previous paper[12]. A 5 mm o.d. NMR sample tube was immersed in a 10mm o.d. NMR tube containing $(CD_3)_2CO$ (Merck). Measurements of ^{17}O NMR spectra were carried out at 13.46MHz on a JEOL JNM-FX 100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller. Typical spectral settings for the measurements of ^{17}O NMR spectra are as follows: 8 K data points, 90° pulse angle corresponding to ca. 10 μs pulse width, 10 kHz spectral width(leading to 2.44 Hz digital resolution), and normally 2000 scans.

3. RESULTS AND DISCUSSION

^{17}O chemical shifts of uranyl oxygens were measured relative to the ^{17}O resonance of $(CD_3)_2CO$ at 5, 15, 25, and 35℃ under the experimental condition that the sum of $[NO_3^-]$ and $[ClO_4^-]$ was constant. The results are enumerated in Table 1. Since there is no interaction of the uranyl ion with perchlorate ion [9], it is considered that the variation of the ^{17}O chemical shifts with the addition of $NaNO_3$ to the aqueous uranyl solution is due to the interaction of the uranyl ion with nitrate ion. As

shown in Fig. 1, the ^{17}O chemical shifts increase almost linearly with $[NO_3^-]$ in its low region but tend to approach a limiting value in its high region. These results can be explained by 1:1 complex formation between uranyl and nitrate ions:

$$UO_2^{2+} + NO_3^- \overset{K}{=} UO_2NO_3^+ \quad (1)$$

Assuming that $[NO_3^-] \gg [UO_2^{2+}]$ and the rate of the equilibrium reaction is very fast compared with the NMR time scale[13], the observed ^{17}O chemical shifts $\delta(^{17}O)_{obsd}$ are given by[14]

$$\delta(^{17}O)_{obsd} = \delta(^{17}O) + \frac{\Delta\delta\, K[NO_3^-]}{1+K[NO_3^-]} \quad (2)$$

where $\delta(^{17}O)$ is the ^{17}O chemical shift of $[UO_2(H_2O)_5]^{2+}$ ion and $\Delta\delta$ is the difference in ^{17}O chemical shift between $[UO_2(H_2O)_5]^{2+}$ and $UO_2NO_3^+$ ions. Equation 2 can be transformed into Eq. 3.

$$\frac{1}{\delta(^{17}O)_{obsd} - \delta(^{17}O)} = \frac{1}{\Delta\delta}\left(1 + \frac{1}{K[NO_3^-]}\right) \quad (3)$$

The plot of $1/((\delta(^{17}O)_{obsd} - \delta(^{17}O))$ against $1/[NO_3^-]$ at 15℃ (Fig. 2) shows a linear relationship, as expected from Eq. 3. The stablility constant K and $\Delta\delta$ at 15℃ were obtained from the slope and intercept in Fig. 2 and are listed along with those at 5, 25, and 35℃ in Table 2.

The positive values of $\Delta\delta$ in Table 2 mean that the ^{17}O resonance of uranyl oxygens of $UO_2NO_3^+$ is at lower field than that of $[UO_2(H_2O)_5]^{2+}$. The lower-field shift of ^{17}O resonance by complexation of nitrate ion is in agreement with the bathochromic shift of electronic absorption bands by the complexation[15] in view of the fact that ^{17}O chemical shifts of uranyl complexes increase as their electronic transition energies decrease[4].

Table 2 shows that stability constants for complex formation of $UO_2NO_3^+$ decrease with temperature, i.e., that the complex formation is exothermic. The stability constants at 25℃

Table 1. The Variation of ^{17}O Chemical Shifts of Uranyl Oxygen Atoms(relative to $(CD_3)_2CO$) with $[NO_3^-]$ at Various Temperatures

$[NO_3^-]$	Temperature/℃			
m	5	15	25	35
0	545.75	546.11	546.38	546.29
0.985	546.11	546.66	546.84	546.84
1.63	546.29	547.02	547.02	547.20
2.04	546.48	547.20	547.20	547.38
2.51	546.66	547.20	547.38	547.56
3.07	546.66	547.56	547.56	547.74
3.79	547.02	547.56	547.92	548.10
4.47	547.02	547.74	547.92	548.28

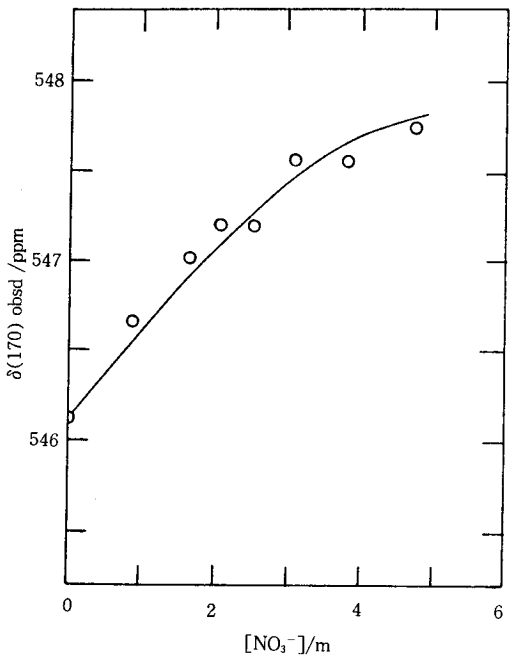

Fig. 1. Dependence of ^{17}O chemical shifts of uranyl oxygen atoms on $[NO_3^-]$ at 15℃. The ^{17}O chemical shift is referred to external $(CD_3)_2CO$: ionic strength=5.0m, $[UO_2^{2+}]$=0.11m, and $[H^+]$=0.08m.

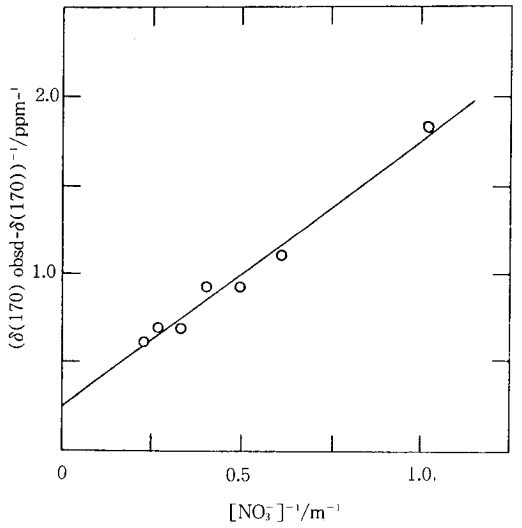

Fig. 2. A plot of $1/(\delta(^{17}O)_{obsd}-\delta(^{17}O))$ against $1/[NO_3^-]$ at 15℃: ionic strength = 5.0m, $[UO_2^{2+}]=0.11$m, and $[H^+]=0.08$m.

Table 2. The Value $\Delta\delta$ and Stability Constants for the Complex Formation of $UO_2NO_3^+$ at Various Temperatures

Temp/℃	$\Delta\delta$/ppm	K/m^{-1}
5	2.3±1.0	0.23 ±0.12
15	4.0±1.0	0.17 ±0.05
25	4.9±2.1	0.10 ±0.04
35	7.9±1.3	0.077±0.013

obtained in this work including the literature values are compiled in Table 3 and likely to depend on the ionic strength in the following manner: they decline with increasing ionic strength, but then pass a minimum(at ca. 5M ionic strength) and rise again in solutions of much higher ionic strengths.

Thermodynamic parameters determined from temperature dependence of the stability constants of $UO_2NO_3^+$ are as follows: $\Delta H=-(27.2\pm1.7)$ kJmol^{-1} and $\Delta S=-(110\pm7)$ JK^{-1}mol^{-1}. The parameters are comparable to those reported by Day and Powers[10]. As shown in Table 4, the parameters diverge considerably for the 1:1 complex formation, which is probably attributed to the difference in the experimental conditions for the 1:1 complex formation. Figure 3 shows the linearity of the

Table 3. Stability Constants for the Complex Formation of $UO_2NO_3^+$ at 25℃

Ionic Strength	K	Method	Reference
0.54 M[a)]	0.37	Electrochemistry	b)
0.82 M	0.20	Electrochemistry	b)
1.06 M	0.19	Electrochemistry	b)
2.00 M	0.24	Distribution	c)
5.0 m	0.10	^{17}O NMR	This work
5.38 M	0.21	Spectrophotometry	d)
6.25 M	0.15	Raman	e)
7 M	0.27	Spectrophotometry	d)

a) 1M=1mol/dm^3, b) Ref. 8, c) Ref. 10, d) Ref. 6, e) Ref. 7.

Table 4. Thermodynamic Parameters on the 1:1 Complex Formation of the Uranyl Ion with Anionic Ligands

Anionic Ligand	ΔH kJ mol^{-1}	ΔS JK^{-1}mol^{-1}	Reference
1. NO_3^-	-27.2	-110	This work
2. NO_3^-	-19.0	-75.3	a)
3. SCN^-	-3.22	3.51	b)
4. $CH_2OHCO_2^-$	5.40	63.2	c)
5. $CH_3CO_2^-$	11.8	86.6	c)
6. $CH_3CO_2^-$	12.8	90.8	d)
7. SO_4^{2-}	9.62	66.9	a)
8. SO_4^{2-}	18.2	95.8	b)
9. SO_4^{2-}	20.8	122	e)
10. Cl^-	15.9	50.2	a)

a) Ref. 10, b) S. Ahrland and L. Kullberg, Acta Chem. Scand., **25**, 3677(1971), c) P. Bernardo, A. Bismondo, R. Portanova, O. Traverso, and L. Magon, Inorg. Chim. Acta, **18**, 47(1976), d) S. Ahrland, Structure and Bonding, **5**, 118(1968), e) A. R. Bailey and J. W. Larson, J. Phys. Chem., **75**, 2368(1971).

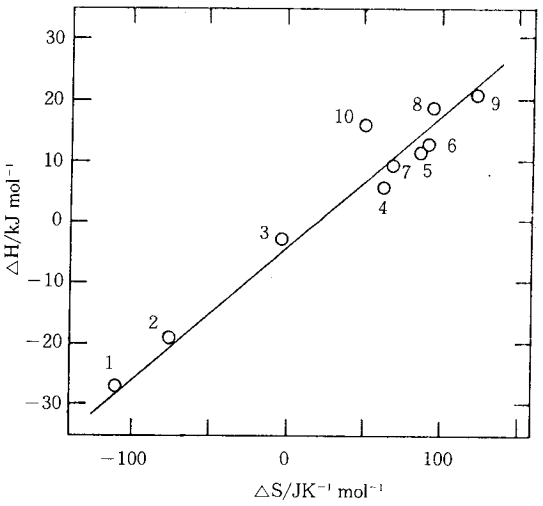

Fig. 3. Correlation between the enthalpy and entropy for 1:1 complex formation of the uranyl ion with anionic ligands. The figures correspond those in Table 4.

relationship between the enthalpy and entropy. Choppin[16] interpreted such a linearity in terms of a model of desolvation plus cation-anion combination: he divided the complex formation into two steps(desolvation and cation-anion combination steps) and stated that the enthalpy and entropy changes are reflective primarily of the desolvation step, while the free energy change is related almost completely to the cation-anion combination step.

The stability constant of $UO_2NO_3^+$ may be determined by ^{14}N NMR spectroscopy because it is expected that the line width of ^{14}N resonance of $UO_2NO_3^+$ ion is different from that of free nitrate ion. But it was impossible to determine the stability constant by this method probably owing to the small difference in the ^{14}N line width between the two ions. From this work ^{17}O NMR spectroscopy proved to be a powerful tool to determine the stability constants of the uranyl ion with weakly interacting ligands.

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