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Oxygen-17 NMR Study of the Uranyl Ion. IV.[1] ^{17}O Nuclear Magnetic Relaxation and Chemical Shifts of Uranyl Oxygen Atoms and Coordinated Water

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^{17}O nuclear magnetic relaxation times and chemical shifts of uranyl oxygen atoms (hereafter uranyl oxygens) and solvent water have been measured with changing concentration of the uranyl ion in aqueous solution. The ^{17}O resonance of the water molecule in the first-coordination sphere is determined to be at 90.1±1.2 ppm relative to free water at 25 °C. The effective correlation time for the ^{17}O quadrupolar relaxation of the coordinated water, which corresponds to the reorientation time for the hydrated uranyl ion, is about 8.7 times that of free water. The ^{17}O spin-lattice relaxation times (T_1) of uranyl oxygens have been measured at 25 °C. From the ^{17}O T_1 values the ^{17}O nuclear quadrupole coupling constant of uranyl oxygens has been estimated to be 0.44 MHz. This small value implies the high symmetry of electron distribution around uranyl oxygens.

Although ^{1}H resonances of the water molecule in the first-coordination sphere of a uranyl ion (UO_2^{2+}) have been observed,[2–5] it is impossible to observe directly the ^{17}O resonance of the coordinated water even at low temperature. The ^{17}O nuclear magnetic relaxation of acidified water is dominated by a quadrupolar relaxation process,[6] which is brought about by interaction of the nuclear electric quadrupole moment with fluctuations of the electric field gradient (EFG) at the oxygen nucleus. The equality of T_1 and T_2 (spin-spin relaxation time) holds for acidic solutions of pure water. In the limit of extreme narrowing, the ^{17}O longitudinal relaxation rate follows Eq. 1,[7]

$$\frac{1}{T_1}=\frac{12\pi^2}{125}\left(1+\frac{\xi^2}{3}\right)\left(\frac{e^2qQ}{h}\right)^2\tau_c, \tag{1}$$

where ξ is an asymmetry parameter of the electric field gradient, e^2qQ/h the quadrupole coupling constant (QCC) in Hz, h the Planck constant, and τ_c the effective correlation time for molecular reorientation. Approximate estimate of τ_c for isotropic tumbling may be made by application of the modified Stokes-Einstein-Debye formula,

$$\tau_c = 4\pi r^3 f\eta/3k_BT, \tag{2}$$

where f is the Gierer-Wirtz microviscosity correction factor,[8] r the molecular radius, η the viscosity, k_B the Boltzmann constant, and T the absolute temperature.

The τ_c value is expected to increase for water coordinated to diamagnetic ions in aqueous solution, thus causing the broadening of the ^{17}O resonance. If the exchange reaction of water between free and coordinated water in the ions is very fast, a single ^{17}O resonance of water is observed, which corresponds to the average of resonances in these environments.

In order to elucidate the behavior of the coordinated water in the uranyl ion, we have measured linewidths and chemical shifts of ^{17}O resonances of solvent water with changing concentration of the uranyl ion in aqueous solution. ^{17}O relaxation times of uranyl oxygens have been also measured and an ^{17}O QCC value of uranyl oxygens has been estimated.

Experimental

Uranyl nitrate hexahydrate $UO_2(NO_3)_2\cdot 6H_2O$ was purified by the extraction into diethyl ether from ammonium nitrate solution and recrystallized twice from aqueous solution. Preparation of uranyl perchlorate pentahydrate $UO_2(ClO_4)_2\cdot 5H_2O$ and ^{17}O-enriched uranyl oxygens has been described elsewhere.[9] The concentrations of uranyl ions were calculated on the assumption that the hydration number of the uranyl ion is 5.[4] The ^{17}O NMR spectra were obtained with a JEOL JNM-FX 100 FT-NMR spectrometer operating at 13.46 MHz. The measurements were performed with a 5-mm o.d. NMR sample tube, which was immersed in a 10-mm o.d. concentric NMR tube containing $(CD_3)_2CO$ (Merck). The samples were not degassed since the presence of oxygen makes no effect on the ^{17}O linewidth.[10]

Full linewidths ($\Delta\nu$) at half height were determined by a least-squares Lorentzian lineshape-fitting procedure. The positive chemical shift is downfield relative to the reference signal. Samples for measurements of ^{17}O linewidths and spin-lattice relaxation times of uranyl oxygens were prepared by the same method as described in the previous paper.[9] The ^{17}O T_1 measurements, which were carried out at 54.10 MHz on a JEOL JNM-GX 400 FT-NMR spectrometer, were made by using the inversion recovery pulse sequence.

Results and Discussion

^{17}O Chemical Shifts of Coordinated Water. ^{17}O chemical shifts of uranyl oxygens relative to solvent water tend to decrease with increasing concentration of the uranyl ion in nitrate solution, as shown in Fig. 1. If one adopts $(CD_3)_2CO$ as a reference for ^{17}O chemical shifts, it is possible to know how the concentration of the uranyl ion affects the respective ^{17}O chemical shifts of uranyl oxygens and solvent water. An example of the results is illustrated in Fig. 2. The ^{17}O chemical shifts of uranyl oxygens increase linearly with increasing concentration of the uranyl ion, where $d\delta(^{17}O)/d[UO_2^{2+}]=1.7$ ppm m^{-1} at 25 °C. This value is larger than that for the uranyl perchlorate complex,[1] and

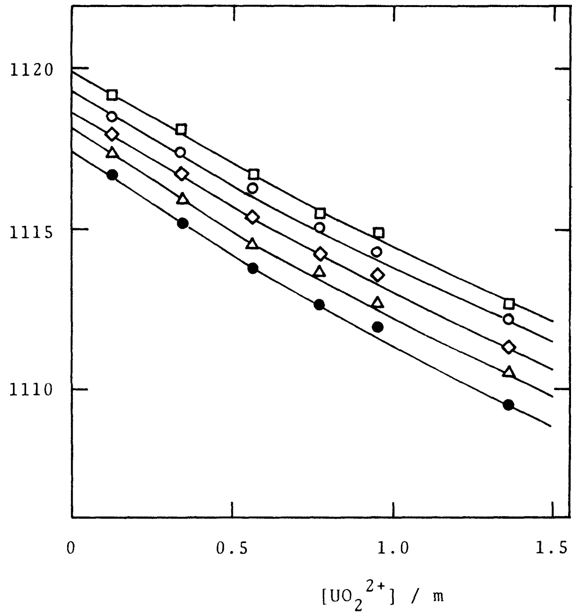

Fig. 1. Dependence of ^{17}O chemical shift of uranyl oxygens (relative to solvent water) on $[UO_2^{2+}]$ in nitrate solution at 20 (●), 25 (△), 30 (◇), 35 (○), and 40 (□)°C; 1 m=1 mol kg^{-1}.

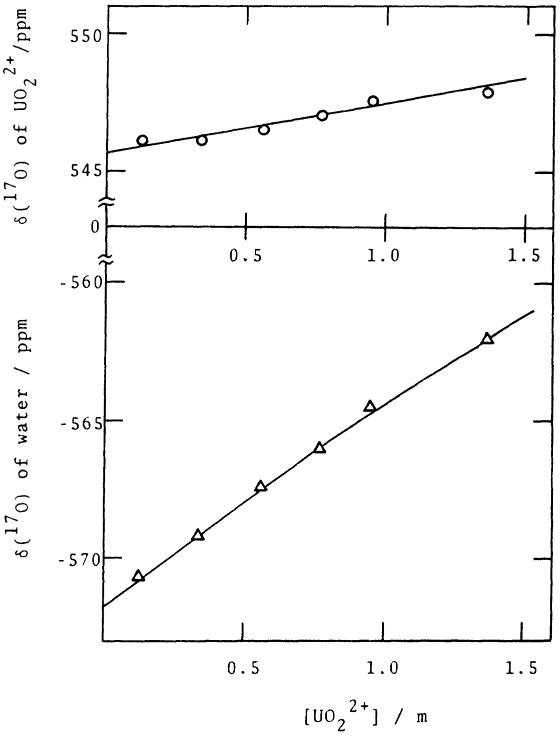

Fig. 2. Effects of $[UO_2^{2+}]$ on ^{17}O chemical shift (relative to acetone-d_6) of uranyl oxygens (○) and solvent water (△) in nitrate solution at 25°C.

this result is attributed to the formation of $UO_2NO_3^+$, the ^{17}O chemical shift of which is larger than that of UO_2^{2+} ion by 4.9 ppm at 25 °C.[1)]

Table 1. ^{17}O Chemical Shifts[a)] and Linewidths of Free and Coordinated Water in the Uranyl Ions at Various Temperature

Temp	$\delta_f(^{17}O)$	$\delta_c(^{17}O)$	$\Delta\nu_f$	$\Delta\nu_c$
°C	ppm	ppm	Hz	Hz
20	−570.6±0.1	−479.6±1.4	53.5±0.5	477±9
25	−571.8±0.1	−481.7±1.1	45.8±0.9	413±16
30	−571.7±0.1	−487.0±1.1	39.7±0.5	339±9
35	−572.4±0.1	−488.9±0.9	34.6±0.1	290±3
40	−573.0±0.1	−491.8±1.6	29.5±0.4	253±7

a) Relative to $(CD_3)_2CO$.

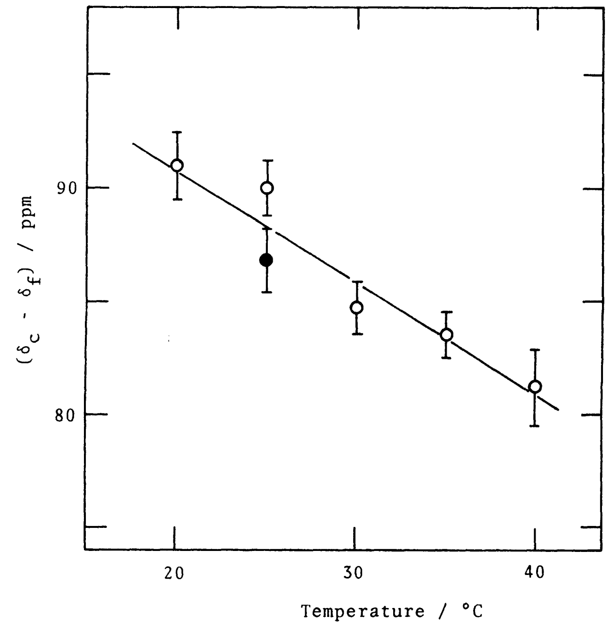

Fig. 3. Temperature dependence of the difference in ^{17}O chemical shift between free and coordinated water in nitrate (○) and perchlorate (●) solutions.

On the other hand, the ^{17}O resonances of solvent water shift downfield and the plot of $\delta(^{17}O)$ vs. $[UO_2^{2+}]$ deviates slightly from a linear relationship with increasing $[UO_2^{2+}]$ as shown in Fig. 2. This arises from the fact that since the exchange of water between free and coordinated water in the uranyl ion is very fast,[2,11)] the observed ^{17}O resonance is the average of the resonances in these environments. The observed ^{17}O chemical shift is given by

$$\delta(^{17}O)_{obsd} = P_f\delta_f(^{17}O) + P_c\delta_c(^{17}O), \qquad (3)$$

where P_f (or $\delta_f(^{17}O)$) and P_c (or $\delta_c(^{17}O)$) are mole fractions (or chemical shifts) of free and coordinated water, respectively. Assuming that the effect of NO_3^- ions on ^{17}O chemical shifts of water is negligible,[12)] we calculated $\delta_f(^{17}O)$ and $\delta_c(^{17}O)$ by a nonlinear least-squares method. The results obtained are listed in Table 1. The ^{17}O chemical shifts of free water relative to $(CD_3)_2CO$ are in good agreement with the literature value.[13)]

Figure 3 shows that the difference in ^{17}O chemical shift between free and coordinated water decreases with increasing temperature. Since $d\delta(^{17}O)/dT$ for

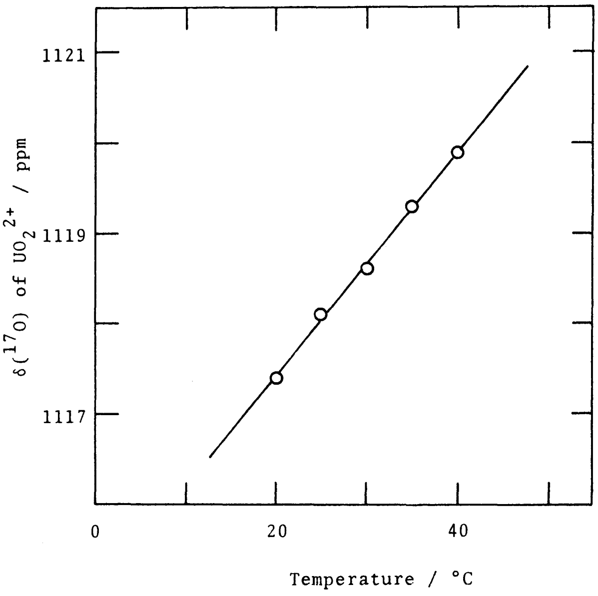

Fig. 4. Temperature dependence of ^{17}O chemical shift of uranyl oxygens (relative to pure water) at infinite dilution of the uranyl ion.

pure water is -0.03 ppm °C^{-1},[12] then $d\delta(^{17}O)/dT$ for the coordinated water was calculated to be 0.52 ppm °C^{-1} from the slope in Fig. 3. The ^{17}O chemical shift of uranyl oxygens relative to free water at infinite dilution of the uranyl ion is given by $(1114.9\pm0.1)+(0.12\pm0.01)\times$Temp (°C) as shown in Fig. 4. The second term agrees with the difference in $d\delta(^{17}O)/dT$ between uranyl oxygens (+0.087 ppm °C^{-1})[1] and pure water.

^{17}O Relaxation Times of Coordinated Water. The dependence of ^{17}O linewidth ($\Delta\nu_{obsd}$) of solvent water on [UO$_2^{2+}$] is shown in Fig. 5. Assuming that the viscosity of the solution studied is equal to that of pure water and the rate of water exchange is slow relative to the rate of molecular reorientation,[14] $\Delta\nu_{obsd}$ is given by

$$\Delta\nu_{obsd} = P_f\Delta\nu_f + P_c\Delta\nu_c, \qquad (4)$$

where $\Delta\nu_f$ and $\Delta\nu_c$ are linewidths of free and coordinated water, respectively. The values of $\Delta\nu_f$ and $\Delta\nu_c$ calculated by a nonlinear least-squares method are listed in Table 1. From the results that the values of $\Delta\nu_f$ and $\Delta\nu_c$ for the nitrate complex agree with those for the perchlorate complex within experimental errors (Fig. 5), the effect of formation of the UO$_2$NO$_3^+$ complex[1] on $\Delta\nu_c$ and $\Delta\nu_f$ is considered to be negligible in the concentration range studied.

Table 1 shows that the $\Delta\nu_f$ values are consistent with linewidths of pure water in the literature[15] within experimental errors and that the average ratio of $\Delta\nu_c$ to $\Delta\nu_f$, $(\Delta\nu_c/\Delta\nu_f)_{av}$, is about 8.7. Since an external charge has only a negligible effect on the ^{17}O electric field gradient of water,[16,17] the ^{17}O QCC and the asymmetry parameter of the coordinated water can be assumed to be the same as those of pure water (QCC=6.68 MHz; ξ=0.93).[16] The $(\Delta\nu_c/\Delta\nu_f)_{av}$ value should be, therefore, equal to the ratio of the tumbling time (τ_c) between coordinated and free water. The τ_c value for the coordinated water can be estimated from Eq. 2 on the assumption that the radius (3.82 Å) of the hydrated uranyl ion is taken to be the sum of the van der Waals radius (1.40 Å) of oxygen and the distance (2.42 Å)[4] between the uranium atom and the water of hydration. The estimated value of τ_c (1.9×10^{-11} s) at 25 °C for the coordinated water is longer than that (2.5×10^{-12} s) for pure water by a factor of 7.6, which is close to $(\Delta\nu_c/\Delta\nu_f)_{av}$. This supports the idea that the effective correlation time for the ^{17}O quadrupolar relaxation of the coordinated water in the uranyl ion corresponds to the reorientation time for the hydrated uranyl ion. It is worth noting that for 2+ diamagnetic ions such as Ca^{2+}, Mg^{2+}, and Cd^{2+}, τ_c for the water molecule in the first-coordination sphere corresponds to intramolecular rotation around the metal-oxygen axis.[18]

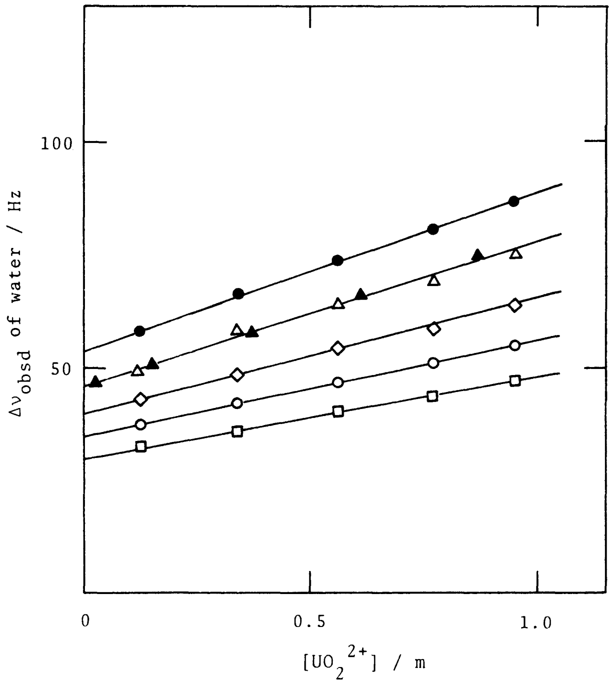

Fig. 5. Dependence of ^{17}O linewidth of solvent water on [UO$_2^{2+}$] in nitrate solution at 20 (●), 25 (△), 30 (◇), 35 (○), and 40 (□)°C; 25°C (▲), in perchlorate solution.

The quadrupolar relaxation rate is usually well represented by an Arrhenius-type function

$$1/T_2 = A\exp(E_Q/RT), \qquad (5)$$

where E_Q is an activation energy for the reorientation. Plots of $\ln\Delta\nu_c$ or $\Delta\nu_f$ vs. $1/T$ were linear in the temperature range studied. The activation energies for free and coordinated water were determined to be 22.4 ± 0.1 and 24.8 ± 0.8 kJ mol^{-1}, respectively.

^{17}O Relaxation Times of Uranyl Oxygens. We measured ^{17}O T_1 relaxation times of uranyl oxygens (enriched by using H$_2$^{17}O (42.1 atom%)) in aqueous

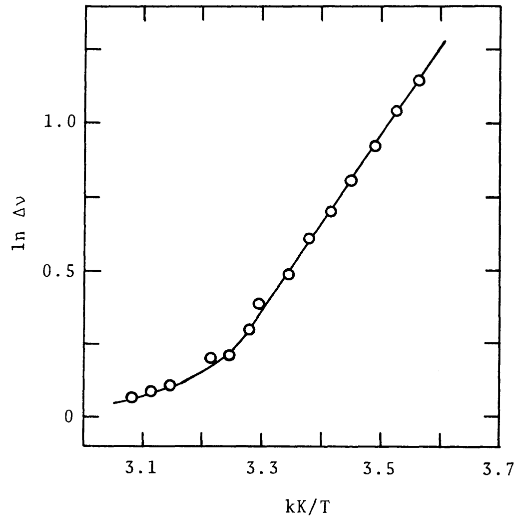

Fig. 6. A semilogarithmic plot of ^{17}O linewidths of uranyl oxygens against the reciprocal temperature. $[UO_2^{2+}]=0.5$ m and $[H^+]=0.1$ m in nitrate solution.

perchlorate solution ($H_2O:D_2O=1:1$ by weight), where $[UO_2^{2+}]=0.098$ m and $[H^+]=0.23$ m. The T_1 values were determined to be 0.245±0.001, 0.227±0.001, and 0.244±0.001 s at 25 °C for $[^{16}O=U=^{17}O]^{2+}$, $[^{17}O=U=^{17}O]^{2+}$, and $[^{18}O=U=^{17}O]^{2+}$, respectively. In view of the fact that three T_1 values become equal with increasing temperature,[19] the slightly smaller T_1 value for $[^{17}O=U=^{17}O]^{2+}$ may be attributed to overlapping of three ^{17}O resonances. When the values of 1.0 cp and 3.82 Å are taken as the viscosity of the solution studied and the molecular radius, respectively, the τ_c value for the hydrated uranyl ion was calculated to be 2.2×10^{-11} s from Eq. 2. The ^{17}O QCC of uranyl oxygens can be obtained from Eq. 1 by using values of T_1 (0.245 s) and τ_c and taking the asymmetry parameter ξ to be zero. The value obtained is 0.44 MHz, which appears to be the smallest of previously measured ^{17}O QCC values. For tetrahedral molecules such as MoO_4^-, RuO_4, and OsO_4, ^{17}O QCC's have been reported to be 0.72,[20] 1.12,[21] and 0.967 MHz,[21] respectively. The significantly small ^{17}O QCC of uranyl oxygens implies the high symmetry of the electron distribution around uranyl oxygen atoms.

We also measured ^{17}O linewidths of a $[^{16}O=U=^{17}O]^{2+}$ isotopomer in aqueous nitrate solution ($H_2O:D_2O=1:2$ by weight), where $[UO_2^{2+}]=0.5$ m and $[H^+]=0.1$ m. Figure 6 shows that an Arrhenius plot of the ^{17}O linewidth against temperature indicates a marked change in the activation energy around 40 °C. This result resembles the results of dynamic behavior of water, e.g. rotational[22] or translational processes,[23] where activation energies for both types of processes decrease with temperature. The activation energy obtained from Fig. 6 is 24.2±0.3 kJ mol^{-1} in the low-temperature range (7—35 °C). The activation energy value is very close to that for ^{17}O quadrupolar relaxation rate of the water molecule in the first-coordination sphere of the uranyl ion, indicating that there is a similarity in ^{17}O quadrupolar relaxation mechanisms between the uranyl oxygens and the coordinated water.

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