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The Rates and Mechanisms of Water Exchange of Actinide Aqua Ions: A Variable Temperature ^{17}O NMR Study of $U(H_2O)_{10}{}^{4+}$, $UF(H_2O)_9{}^{3+}$, and $Th(H_2O)_{10}{}^{4+}$

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The rate constants and the activation parameters for the exchange between water solvent and $[U(H_2O)_{10}]^{4+}$ and $[UF(H_2O)_9]^{3+}$, and a lower limit for the rate constant at room temperature for $[Th(H_2O)_{10}]^{4+}$, were determined by ^{17}O NMR spectroscopy in the temperature range 255−305 K. The experiments were made at different constant hydrogen ion concentrations, which varied between 0.16 and 0.8 mol kg^{-1}. The Th(IV) system was investigated using Tb^{3+} as a shift reagent. The following kinetic parameters at 25 °C were obtained: $k_{ex} = (5.4 \pm 0.6)\ 10^6\ s^{-1}$, $\Delta H^{\ddagger} = 34 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -16 \pm 10$ J mol^{-1} K^{-1} for U^{4+}(aq), $k_{ex} = (5.5 \pm 0.7)\ 10^6\ s^{-1}$, $\Delta H^{\ddagger} = 36 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = 3 \pm 15$ J mol^{-1} K^{-1} for UF^{3+}(aq), and $k_{ex} > 5\ 10^7\ s^{-1}$ for Th^{4+}(aq), where the uncertainty is given at the 2σ-level. This is the first experimental information on the kinetic parameters for the exchange of water for any M^{4+} ion. There is no information on the rates and mechanisms of ligand substitutions involving other mono-dentate ligands, hence the mechanistic interpretation of the data is by necessity provisional. The kinetic data and the known ground-state geometry with a coordination number of 10 ± 1 for the Th(IV) and U(IV) complexes suggest a dissociatively activated interchange mechanism. There is no noticeable effect of coordination of one fluoride or one hydroxide to U(IV) on the water exchange rate. This is unusual, for other metal ions there is a strong labilizing of coordinated water when a second ligand is bonded, e.g., in complexes of aluminum and some d-transition elements. In previous studies of the rates and mechanisms of ligand exchange in uranium(VI) systems we found a strong decrease in the lability of coordinated water in some fluoride containing complexes.

Introduction

In a previous communication[1] dealing with the water exchange in $UO_2{}^{2+}$(aq), we have given a summary of the experimental methods used to study the exchange in metal ion water systems; the procedures are described in more detail by Cossy et al.,[2] Powell and Merbach,[3] and Bleuzen et al.[4] The present study focuses on the rates, activation parameters, and mechanisms of water exchange between U^{4+}(aq), Th^{4+}(aq), and UF^{3+}(aq) and solvent water. No experimental data of this type are available for any M^{4+} aqua ions. A key point will be to explore if the water exchange follows a predominantly associative (I_a) or a dissociative (I_d) interchange mechanism. Because of the very few experimental data available, the mechanistic discussion will be provisional and has to rely on our own kinetic data and information on the coordination number of U(IV) and Th(IV) in aqueous solution.[5] The water exchange for both the paramagnetic U^{4+}(aq) and the diamagnetic Th^{4+}(aq) ions was studied using ^{17}O NMR relaxation, where the transverse and longitudinal relaxation rates of the bulk water signal contain information on the exchange rate. The Th^{4+}(aq) system was studied using Tb^{3+}(aq) as a chemical shift reagent.

Previous studies of water exchange in aluminium and some d-transition metals show that water is strongly labilized by coordinated of hydroxide,[6] fluoride[7] and other ligands.[8] In the previous study we have discussed the rates of water exchange in the uranyl(2+) aqua ion and some of its complexes, in particular how this is effected by the presence of coordinated fluoride. We will therefore explore if the rate constants for water exchange varies between the M(IV) aquo ions and their complexes, using UF^{3+}(aq) as a model.

Experimental Section

Preparation of Stock Solutions. $U(ClO_4)_4$ solutions were prepared by electrolysis from an acidified $UO_2(ClO_4)_2$ solution, using a two compartment cell with separated mercury cathode and platinum anode, at a potential of 4 V.[9] After completed electrolytic reduction, the solution was left in air for some minutes to allow oxidation of the trace amounts of U(III) formed. The solution was then stored under argon. The total concentration of uranium was known from the added uranium but was also checked spectrophotometrically after oxidizing the U(IV) to $UO_2{}^{2+}$ with concentrated HNO_3. The U(IV) content was determined by a redox titration using an excess of permanganate, which was then back-titrated iodometrically.[10] $Th(ClO_4)_4$ was prepared from $Th(OH)_4$ as described previously.[11] $Tb(ClO_4)_3$ solutions were prepared by dissolving terbium oxide in warm perchloric acid using moderate heating, followed by EDTA titration using a hexamethylene-tetramin buffer and xylenol orange as indicator.[12]

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TABLE 1: Kinetic Data for Aqua Metal Ions

ion	K_{ex}/s^{-1} at 298 K	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/Jmol^{-1}K^{-1}	$(A/h)/10^5$(rad/s)	$-C/10^9$(K^2 rad/s)
$^aU^{4+}$	$(4.8 \pm 0.8) \times 10^6$	31 ± 3	-12 ± 13	9.8 ± 0.3	2.5 ± 0.5
$^bU^{4+}$	$(6.0 \pm 0.1) \times 10^6$	39.2 ± 0.6	16 ± 2	9.9 ± 0.3	4.0 ± 0.65
$^cU^{4+}$	$(5.0 \pm 1.0) \times 10^6$	32 ± 4	-9 ± 16		
$^dU^{4+}$	$(6.1 \pm 0.2) \times 10^6$	39.6 ± 0.9	18 ± 3		
$^eU^{4+}$	$(5.4 \pm 0.6) \times 10^6$	34 ± 3	-16 ± 10		
$^fU^{4+}$	$(6.2 \pm 0.3) \times 10^6$	37 ± 1.7	10 ± 5		
$^gUF^{3+}$	$(4.4 \pm 4.8) \times 10^6$	36 ± 32	2 ± 120	11.1 ± 0.8	8 ± 2
$^hUF^{3+}$	$(5.5 \pm 0.7) \times 10^6$	35.7 ± 4.4	3 ± 15	9.9 ± 0.3	9.8 ± 0.6
$^iTh^{4+}$	$>5 \times 10^7$				

[a] Result for fitting data obtained at 11.7 T in the temperature range from 255 to 327 K. [b] Result obtained for fitting data obtained at 18.8 T in the temperature range from 255 to 327 K [c] Result obtained for fitting data obtained at 11.7 T in the temperature range 255 to 305 K. [d] Result obtained for fitting data obtained at 18.8 T in the temperature range 255 to 305 K. [e] Result obtained for fitting data obtained at 11.7 T and 18.8 T, both magnetic fields in the temperature range from 255 to 305 K using individual weights. [f] Result obtained for fitting data obtained at 18.8 T in the temperature range from 255 to 327 K using equal weights. [g] Result obtained for fitting data obtained at 11.7 T in the temperature range from 268 to 302 K using individual weights. [h] Result obtained for fitting data obtained at 18.8 T in the temperature range between 268 to 302 using individual weights. [i] Result obtained for fitting data obtained at 18.8 T. Errors are given as 2σ.

NMR Sample Preparations. The ionic medium had a constant perchlorate concentration of 4 mol/kg, the concentrations of the cations Na^+, H^+, U^{4+}, and Th^{4+}varied as described in the Supporting Information. The acidity was adjusted with $HClO_4$, and the concentration of fluoride by adding NaF. The samples contained 5−8% D_2O and 5% $H_2{}^{17}O$ (36% enrichment). The test solutions were prepared by weight and their concentrations are given in mol/kg water (m).

NMR Measurements. The ^{17}O NMR spectra were obtained with Bruker DMX-800 (18.8 T), Bruker DMX-500 (11.7 T), and Bruker AM 400 (9.4 T) spectrometers, using 5 mm tubes, in the terbium experiments using solutions withthout lock. The temperature was varied using the Bruker Eurotherm variable temperature control unit, calibrated against methanol.[13] The longitudinal relaxation rates were measured by the inversion recovery method. The transverse relaxation rates were obtained from the line width determined by Lorentzian fitting of the peaks. The Carr−Purcell−Meiboom−Gil method could not be used as the pulse length was comparable to the transverse relaxation rate. The chemical shifts are given relative to that of the water signal in the corresponding ionic medium. The rate of water exchange in U^{4+}(aq) and UF^{3+}(aq) was determined from the temperature dependence of these parameters, in solutions with and without U^{4+}. The water exchange in the Th^{4+} system was determined according to the litereture[4] as described in the previous study.[1] All experimental data are given in Supporting Information, Table S1.

Results

Data Treatment. *U(IV) Systems.* The terminology used in the following section is the same as in refs 1−4. In these papers the effect of paramagnetic Tb^{3+}(aq) in small population on the longitudinal and transverse relaxation rates and the chemical shift of bulk water were discussed. Some approximations are necessary in order to calculate the rate of water exchange from the experimental data,[1] and we suggest that the same approximations can be used also for U^{4+}(aq) (see Appendix). The extreme narrowing limit is valid for all the water molecules in the solution, i.e., the difference between their transverse and longitudinal relaxation rates, (i) $(1/T_{1A} - 1/T_{2A})$ for the bulk, (ii) $(1/T_{2os} - 1/T_{1os})$ for the water coordinated in the outer coordination sphere, (iii) $(1/T_{2m} - 1/T_{1m})$ for the water coordinated in the inner coordination sphere, is close to zero and negligible. Also the chemical shift of the water in the outer coordination sphere $\Delta\omega_{os}$, is negligible compared to that of the inner coordination sphere $\Delta\omega_m$ as shown by Cossy et al.[2] for lanthanide (3+) ions. For U^{4+} ion we verified that these terms could be neglected, $(1/T_{1A} - 1/T_{2A})$ experimentally, and the others by the calculation described in the Appendix. Hence, for the U^{4+} water exchange system, only the "kinetic term" remains:

$$\frac{1}{T_2} - \frac{1}{T_1} = P_{U^{4+}} \frac{\Delta\omega^2_{rU^{4+}}}{k_{exU^{4+}}} \tag{1}$$

$$\Delta\omega_{rU^{4+}} = \frac{\Delta\omega}{P_{U^{4+}}} \tag{2}$$

$\Delta\omega$, $1/T_2$, and $1/T_1$ are the chemical shift in radians relative to water, the transverse and longitudinal relaxation rates measured in a solution containing U^{4+}, respectively. These data are available as Supporting Information. $P_{U^{4+}}$ is the mol fraction of water coordinated to the paramagnetic ion, calculated using the coordination number 10 for U^{4+}(aq),[5] $\Delta\omega_{rU^{4+}}$ (in the following denoted $\Delta\omega_r$) is the reduced chemical shift in radians, $k_{exU^{4+}}$ (in the following denoted k_{ex}) is the rate constant for the specific water exchange between the water coordinated to U^{4+} and the bulk.

Equations 1 and 2 were used to calculate k_{ex}, the rate constant for the exchange between water coordinated to U^{4+} ion and the bulk. The activation parameters $\Delta H^‡$ and $\Delta S^‡$ were determined from the experimental rate constants using eq 3. Alternatively one may determine $\Delta H^‡$ and the rate constant for the exchange at 25 °C, k_{ex}^{298}, using eq 4.

$$k_{ex} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^‡}{R} - \frac{\Delta H^‡}{RT}\right) \tag{3}$$

$$k_{ex} = \frac{k_{ex}^{298} T}{298.15} \exp\left(\frac{\Delta H^‡}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right) \tag{4}$$

The hyperfine coupling constant for U^{4+}(aq) was calculated from eq 5, by fitting the temperature vs $\Delta\omega_r$ data

$$\Delta\omega_r = \frac{2\pi B g_L (g_L - 1) J (J+1) \mu_B}{3 k_B T} \frac{A}{h} + \frac{C}{T^2} \tag{5}$$

B is the static magnetic field, g_L (0.812 for U^{4+}) the isotropic Landé factor, J (4 for U^{4+}) the electron spin angular momentum quantum number, μ_B the Bohr magneton, A/h the hyperfine coupling constant[2], and C an empirical constant. The term C/T^2 gives a slight improvement of the fit, but has no well-established physical significance. The hyperfine coupling constant given in Table 1 is practically the same for the different magnetic fields used.

The experimental quantity ($1/T_1 - 1/T_2$) increases with decreasing temperature. Hence systematic errors, e.g., field inhomogeneity, are expected to be larger at higher temperature. A measure of the importance of errors of this type is obtained by comparing the value of $(1/T_2 - 1/T_1)/P_{U^{4+}}$ at different magnetic fields. The data given in Supporting Information, Table S2, shows that there are significant deviations between the ratio of the magnetic fields and the ratio of the measured values of $(1/T_2 - 1/T_1)/P_{U^{4+}}$. The deviations are larger at higher temperature and for the data obtained at 9.4 T. For the data at 11.7 T above 300 K the expected ratio, $(^8/_5)^2 = 2.56$, can be reached by subtracting a temperature-dependent inhomogeneity term, which varies between 4 and 12 Hz in the measured $1/T_2$, from $(1/T_2 - 1/T_1)/P_{U^{4+}}$ measured at 11.7 T. A systematic error of 5 Hz in the 11.7 T data brings the experimental data at 11.7 and 18.8 T much closer together. However, we abstain from data "polishing" and use the experimental information as described in the following. The measurements at 9.4 T were obtained using a 5 mm tube in a 10 mm probe-head, which might have an adverse effect on the homogeneity of the field, therefore we used only the data at the two higher magnetic fields when calculating the rate of exchange. To test the effect of inhomogeneity on the numerical values of the parameters we made different evaluations: using weighted data, by assigning equal weight to all experimental points, using each series of measurements at different magnetic fields separately, or by lumping the series together. The ratio of $(1/T_2 - 1/T_1)/P_{U^{4+}}$ for the two different magnetic fields were close to the expected value at temperatures below 303 K. We therefore made an evaluation of the rate parameters using these data alone. The individual weight for an experimental point, i, is $w_i = 1/\sigma_i^2$, where σ_i is the estimated uncertainty. The combined effect of a 5 Hz inhomogeneity term, a 3% error in $\Delta\omega_r$ and a 2−8% error due to data treatment in ($1/T_1 - 1/T_2$) results in an error that varies between 7 and 70% in the value of k_{ex}, from the lowest to the highest temperature.

The kinetic results are given in Table 1. The parameter values obtained when using equal and individual weights were the same for each series, but the standard deviation for the latter was lower. By giving zero weight to the experimental data above 303 K we also obtained similar results for each series measured at different fields. Both the absolute values and the estimated uncertainty of the kinetic parameters for the two magnetic fields differ from each other. In the case of the series measured at 18.8 T we obtained a 20% higher value for both the rate constant and the activation enthalpy, and a small positive activation entropy, while a small negative activation entropy was obtained for the data at 11.7 T. The standard deviations at 18.8 T are also significantly lower. The "best" set is the one from the combined data up to 305 K obtained at 18.8 and 11.7 T. The kinetic parameters using this set are $k_{ex} = (5.4 \pm 0.6)\ 10^6\ s^{-1}$, $\Delta H^{\ddagger} = 34 \pm 3$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -16 \pm 10$ JK^{-1} mol^{-1}, where the uncertainty is given at the 2σ level. The temperature dependence of the measured rate constant together with the estimated errors is given in the Figure. Data measured at 11.7 T, obtained from solutions containing $[U^{4+}] = 0.05$, $[H^+] =$ 0.79 m, $[ClO_4^-] = 4$ m are shown as "Δ". Data measured at 9.4 T, obtained from a solution containing $[U^{4+}] = 0.055$ m, $[H^+] = 0.8$ m, and $[ClO_4^-] = 4$ m are shown as "◇". The data from a solution containing $[U^{4+}] = 0.054$, $[H^+] = 0.77$ m, $[ClO_4^-] = 3.9$ m, measured at 18.8 T, are shown as "×". The rate constants obtained from the above data measured at 11.7 T and corrected for inhomogeneity are shown as "○", cf. p 7. Some points measured at 11.7 and 18.8 T are shown with error bars. "□" denotes the data measured at $[H^+] = 0.16$ m. "—" denotes the data measured at 11.7 T in a solution containing $[U^{4+}] = 0.048$ m, $[F^-] = 0.017$ m, $[H^+] = 0.82$ m, $[ClO_4^-] =$ 3.8 m, and "●" denotes data measured at 18.8 T in a solution with $[U^{4+}] = 0.038$ m, $[F^-] = 0.017$ m, $[H^+] = 0.8$ m, and $[ClO_4^-] = 3.8$ m. The full-drawn curve is the fit to the data measured at 18.8 and 11.7 T in the temperature range 255−305 K. The dashed line is the extrapolation to higher temperatures using the parameters obtained in the fit. It describes most of the experimental data within the estimated uncertainty range. The relaxation rates and chemical shifts were measured at different concentrations of H$^+$. No variation was found when $[H^+]$ was varied between 0.16 and 0.8 mol kg^{-1}, even though the concentration of UOH^{3+} varies between 14 and 3% in this $[H^+]$ range.

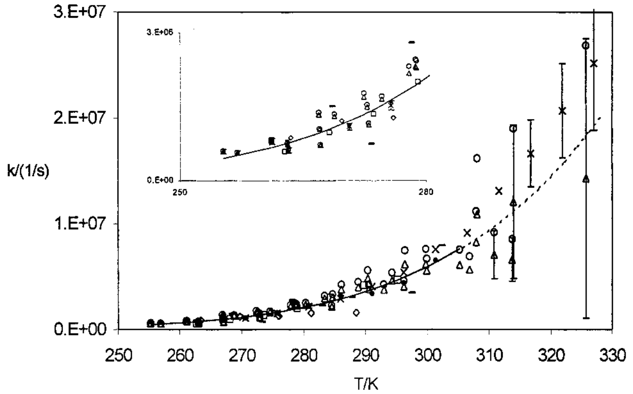

Figure 1. The experimental and calculated temperature dependence of the exchange rate constant for water exchange in U^{4+}(aq) solutions, for notation see text.

We also made measurements at 18.8 and 11.7 T in U^{4+} solution containing 35% UF^{3+}(aq) to examine the effect of complex formation on the water exchange. The samples measured at 18.8 T were prepared in our laboratory and then transported by air to Germany. When analyzing these data we found indications for partial oxidation of U^{4+}. After careful measurements at 11.7 T on our own spectrometer, we could conclude that the U^{4+} solution is much more sensitive toward oxidation in the presence of F^-, than in pure U^{4+}(aq) solutions. Using the reduced chemical shift of UF^{3+}(aq) obtained at 11.7 T it was possible to determine that 20% of the uranium(IV) had been oxidized at the time when the solutions were measured at 18.8 T. The data could be salvaged because the presence of uranyl ion does not disturb the system, but the concentration of U(IV) must be corrected for the amount oxidized. The fluoride data were then treated in the same way as for the U^{4+}(aq). At the concentration used practically all fluoride is coordinated to U^{4+}, forming $UF(H_2O)_9^{3+}$.[5,13] Using the U^{4+}/UF^{3+} ratio, the reduced chemical shift and the water exchange rate constant for U^{4+}(aq), the $\Delta\omega_r$ and the k_{ex} for UF^{3+}(aq) was calculated from the measured values which are averages for the water coordinated to the two ions, the results are given in Table 1. The uncertainty obtained for the series at 11.7 T is very large. However, the series at 18.8 T gives more precise values, $k_{ex} =$ $(5.5 \pm 0.7) \times 10^6\ s^{-1}$, $\Delta H^{\ddagger} = 36 \pm 4$ kJ mol^{-1}, and $\Delta S^{\ddagger} =$ 3 ± 15 J mol^{-1} K^{-1}, which are practically the same as those for U^{4+}(aq).

Th(IV) System. To examine the water exchange of the diamagnetic Th^{4+}(aq), we followed the same method as described for UO_2^{2+}(aq)[1]. In Tb^{3+} solutions without thorium ion the water signal is the average of "free" and coordinated water and the following equations analogous to eq 1 and eq 2 are valid:[2−4]

$$\frac{1}{T_2} - \frac{1}{T_1} = P_{\mathrm{Tb}^{3+}} \frac{\Delta\omega_{\mathrm{rTb}^{3+}}^2}{k_{\mathrm{exTb}^{3+}}} \tag{6}$$

$$\Delta\omega_{\mathrm{rTb}^{3+}} = \frac{\Delta\omega}{P_{\mathrm{Tb}^{3+}}} \tag{7}$$

In the presence of Th^{4+} ion the exchange between the paramagnetic solvent and the first coordination sphere of Th^{4+} may also contribute, and a second exchange term must be added to eq 6:

$$\frac{1}{T_2} - \frac{1}{T_1} = P_{\mathrm{Tb}^{3+}} \frac{\Delta\omega_{\mathrm{rTb}^{3+}}^2}{k_{\mathrm{exTb}^{3+}}} + P_{\mathrm{Th}^{4+}} \frac{k_{\mathrm{exTb}^{4+}}\Delta\omega^2}{k_{\mathrm{exTh}^{4+}}^2 + \Delta\omega^2} \tag{8}$$

Equation 8 in the form

$$Y = \frac{1}{T_2} - \frac{1}{T_1} - P_{\mathrm{Tb}^{3+}} \frac{\Delta\omega_{\mathrm{rTb}^{3+}}^2}{k_{\mathrm{exTb}^{3+}}} = P_{\mathrm{Th}^{4+}} \frac{k_{\mathrm{exTh}^{4+}}\Delta\omega^2}{k_{\mathrm{exTh}^{4+}}^2 + \Delta\omega^2} \tag{9}$$

was used to evaluate the experimental data. There was no significant effect of Th^{4+} on the relaxation rate difference of water in Tb^{3+} solutions, even at high Tb^{3+} and Th^{4+} concentrations. Hence, we have to restrict the discussion to the data obtained at 18.8 T, *cf* Supporting Information Table S1. The value of Y is at most 4% of the measured $1/T_2$, which is not enough to determine the rate constant for the exchange. However, we can estimate a lower limit for the rate constant for the water exchange of Th^{4+} at room temperature. We know that $\Delta\omega$ is about 2×10^5 rad/s and $P_{\mathrm{Th}^{4+}}$ is 0.03; if we assume that 30 Hz is the lowest value of Y that can be measured, we obtain a minimum value of $k_{\mathrm{exTh}^{4+}} > 5 \times 10^7\ \mathrm{s}^{-1}$ at 25 °C.

Discussion

The kinetic parameters for the water exchange of U^{4+}(aq) at 25 °C are $k_{\mathrm{exU}^{4+}} = (5.4 \pm 0.6) \times 10^6\ \mathrm{s}^{-1}$, $\Delta H^\ddagger = 34 \pm 3$ kJ mol^{-1}, and $\Delta S^\ddagger = -16 \pm 10$ JK^{-1} mol^{-1}, and for UF^{3+}(aq) $k_{\mathrm{ex}} = (5.5 \pm 0.7) \times 10^6\ \mathrm{s}^{-1}$, $\Delta H^\ddagger = 36 \pm 4$ kJ mol^{-1}, $\Delta S^\ddagger = 3 \pm 15$ J mol^{-1} K^{-1}. In the case of Th^{4+}(aq) we could only determine a minimum value for the rate constant at room temperature: $k_{\mathrm{exTh}^{4+}} > 5 \times 10^7\ \mathrm{s}^{-1}$ at 25 °C. No experimental data on the solvent exchange are available for U^{4+} or Th^{4+}, or any other M^{4+} aqua ions, therefore we could only use structure information on U^{4+}(aq), $UF(aq)^{3+}$, and Th^{4+}(aq), together with the activation parameters obtained in this study, to judge if the mechanism of the water exchange in these systems follows a dissociative or an associative interchange mechanism. In a previous study[5] we have determined the bond distances within the Th(IV) and U(IV) aqua ions and their first fluoride complexes. We have also determined their coordination number, $n = 10 \pm 1$, using EXAFS data and comparisons with structures of lanthanides with known coordination numbers.

When considering the most probable coordination number in the transition state for the water exchange reaction for M^{4+}(aq) ions one has to note that there are no known complexes with unidentate ligands with a coordination number larger than ten. The most common coordination number is eight or nine. For ten-coordination, this fact makes a limiting associative mechanism (A) unlikely, while a dissociative mechanism (D) is possible. For nine coordination both A and D are possible. There is no evidence for the formation of an intermediate and we therefore have to classify the water exchange in the interchange category, I_a or I_d. As the free energy of reaction for solvent exchange reactions is zero, it follows that the profile of the free energy of activation along the reaction coordinate must be symmetric. The only difference between transition states of I_a, and I_d is that the bond distance between M(IV) and the entering and leaving water is longer in the latter case. This suggests that the water exchange, in a ten-coordinated M^{4+}(aq), most likely takes place via a dissociative interchange mechanism, because this involves smaller steric repulsions between the ligands in the transition state. If the ground-state coordination number is nine instead of ten, we have a ten-coordinate transition state, e.g., with a bicapped Archimedean antiprism geometry, making both I_a and I_d mechanisms possible. The activation entropy has been used as an indicator of the intimate mechanism, but it is affected by interactions beyond the first coordination sphere[15] and therefore difficult to interpret. The only possibility to obtain more precise information about the intimate mechanism of the water exchange seems to be measurements of the activation volumes for the reactions.[2−4]

Ligands coordinated to a metal ion generally labilize the solvent molecules in the first coordination sphere, the effect is often pronounced when hydroxide is coordinated,[6] but also for other ligands such as fluoride[7] and oxalate.[8] No such increase in the lability of coordinated water is indicated here, neither for $U(OH)^{3+}$(aq) nor for UF^{3+}(aq). Matters are different in the uranium(VI) systems,[1] where there was a large decrease in the rate of water substitution in the fluoride containing complexes. One important difference between these systems and the one investigated here is that all water ligand in the uranium(VI) systems might be hydrogen bonded to fluoride, which is not the case in $UF(H_2O)_9{}^{3+}$. This may explain why the rate constant, the activation parameters and the exchange mechanism are similar in UF^{3+}(aq) and U^{4+}(aq).

The rate constant for the water exchange in Th^{4+}(aq) is at least 1 order of magnitude larger than for U^{4+}(aq), possibly related to the difference in the strength of the ion−dipole interactions between M^{4+} and water. In the lanthanides one finds that the rate of water exchange increases with increasing ionic radius for the eight coordinated ions. A similar increase of the rate of substitution with decreasing charge and increasing ionic radius is also found for main group metal ions.[15]

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Appendix

The interpretation of the ^{17}O NMR relaxation data rests on the assumption that the *kinetic term* gives the predominant contribution. In the following we will explore if this assumption is or is not valid in the U^{4+}−water system. The procedure is the same as that described previously by Powell and Merbach[3] for the water exchange of Pr^{3+}(aq) and Nd^{3+}(aq). Table S3 in Supporting Information describes the spectroscopic and magnetic properties of ^{238}U, ^{141}Pr, and ^{17}O isotopes used for the relaxation rate estimations below.

The measured difference between the transverse and longitudinal relaxation rate is

$$\frac{1}{P_m}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=\frac{\Delta\omega^2}{k_{ex}}+\left(\frac{1}{T_{2m}}-\frac{1}{T_{1m}}\right)+\left(\frac{1}{T_{2os}}-\frac{1}{T_{1os}}\right) \quad (A1)$$

Equation A1 can be simplified to eq 1, using the approximations described in the previous paper.

According to the current theory of nuclear relaxation the outer and inner sphere relaxation mechanisms are very similar, indicating the existence of an extreme narrowing limit. As the outer sphere relaxation rates are very small, the third term on the right hand side of eq A1 is much smaller then the other two terms.[2,16] The reason is that the main components in the relaxation are the scalar coupling (denoted with subscript sc) between the oxygen nucleus and the metal ion electron spin and the dipole−dipole interaction (dd) between the bulk water and the metal ion. Both interactions are negligible because they are functions of the distance between the metal ion and the oxygen[3] Equation A1 is then

$$\frac{1}{P_m}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)=\frac{\Delta\omega^2}{k_{ex}}+\left(\frac{1}{T_{2m}}-\frac{1}{T_{1m}}\right) \quad (A2)$$

It is not obvious that the relaxation of coordinated water can be neglected. In order to estimate its contribution we have made a comparison between U^{4+} and Pr^{3+}, which have similar size and the same spin−orbit angular momentum quantum number (J). For Pr^{3+} Powell and Merbach[3] made a detailed calculation and verified that the term $(1/T_{2m} - 1/T_{1m})$ in eq A2 could be neglected. Both types of relaxation have four components:

$$\frac{1}{T_{1m}}=\frac{1}{T_{1q}}+\frac{1}{T_{1dd}}+\frac{1}{T_{1Cs}}+\frac{1}{T_{1sc}} \quad (A3)$$

$$\frac{1}{T_{2m}}=\frac{1}{T_{2q}}+\frac{1}{T_{2dd}}+\frac{1}{T_{2Cs}}+\frac{1}{T_{2sc}} \quad (A4)$$

and we have calculated their magnitude at 67.8 MHz. The first terms on the right hand side of the two equations are relaxations governed by the interaction of the nuclear quadrupole moment and the electric field. The expression for the difference of the transverse and longitudinal relaxation can only be given an explicit expression in the *extreme narrowing limit*. This is

$$\frac{1}{T_{1q}}=\frac{1}{T_{2q}}=\frac{3\pi}{10}\,\frac{2I+3}{I^2(2I-1)}\chi^2(1+\eta^{2/3})^{1/2}\tau_c \quad (A5)$$

If this condition is not fulfilled, eq A5 provides a good starting point for the principal components of this type of relaxation. The nuclear spin $I = {}^5/_2$ for oxygen and the term $\chi^2(1 + \eta^{2/3})^{1/2}$, containing the quadrupolar coupling constant and an asymmetry parameter, are independent of the metal ion and therefore the same for U^{4+} and Pr^{3+}. The rotation (or reorientation) correlation time τ_c of the aqua ions may, however, be different. The condition to obtain the *extreme narrowing limit* is

$$\omega_I^2\tau_c^2 \ll 1 \quad (A6)$$

where τ_c can be estimated from the Stokes−Einstein equation:

$$\tau_c=\frac{4\pi a^3\eta}{3k_BT} \quad (A7)$$

where a is the (hydrodynamic) radius of the aqua ion. Cossy et al.[2] use 400 pm as an average value for a, from which they obtain $\tau_c = 4 \times 10^{-10}$ s at 253 K. If we instead use the U^{4+}−water distance $a = 240$ pm, determined from EXAFS data,[5] we obtain $\tau_c = 1 \times 10^{-10}$ s at 265 K and $\tau_c = 8 \times 10^{-11}$ s at 325 K. Hence, $\omega_I^2\tau_c^2 = 5 \times 10^{-5}$ at 67.8 MHz. If a is twice as large, we obtain $\tau_c = (6-8) \times 10^{-10}$ s, and $\omega_I^2\tau_c^2 = 5 \times 10^{-3}$. These numbers have the same magnitude as for Pr^{3+}, and we can then expect that the relaxation of coordinated water contributes about 7 Hz at 265 K and 1 Hz at 325 K.

The second terms in eqs A3 and A4 are due to the interactions between the nuclear dipole of oxygen and the electronic spin of the metal ion. According to Kowalevski,[17] the relaxation rates are

$$\frac{1}{T_{1dd}}=\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\hbar^2\gamma_I^2\gamma_s^2}{r^6}J(J+1)\left(6\tau_{d1}+14\frac{\tau_{d2}}{1+\omega_s^2\tau_{d2}^2}\right) \quad (A8)$$

$$\frac{1}{T_{2dd}}=\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\hbar^2\gamma_I^2\gamma_s^2}{r^6}J(J+1)\left(7\tau_{d1}+13\frac{\tau_{d2}}{1+\omega_s^2\tau_{d2}^2}\right) \quad (A9)$$

and their difference is

$$\frac{1}{T_{2dd}}-\frac{1}{T_{1dd}}=\frac{1}{15}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\hbar^2\gamma_I^2\gamma_s^2}{r^6}J(J+1)\left(\tau_{d1}-\frac{\tau_{d2}}{1+\omega_s^2\tau_{d2}^2}\right) \quad (A10)$$

where $\omega_s = \gamma_sB$ is the electron resonance frequency, $\gamma_s = g_L\mu_B/\hbar$ the electron gyromagnetic ratio, γ_I the nuclear gyromagnetic ratio for ^{17}O, and r the effective distance between the electron charge and the ^{17}O nucleus, equal to 240 pm as above. τ_{dj} is the correlation time for dipole−dipole interaction:

$$\frac{1}{\tau_{dj}}=k_{ex}+\frac{1}{T_{je}}+\frac{1}{\tau_c} \quad (A11)$$

The dominant term in eq A11 is $1/T_{je}$, which for lanthanides is of the order of magnitude 10^{13} s^{-1}, the electron relaxation rate contribution to the dipole−dipole correlation time can be neglected.

The third terms in eqs A3 and A4 are due to the Curie spin relaxation mechanism (index Cs), which results from the interaction between the nuclear dipole and the static magnetic field of the paramagnetic center. It contains the same quantities as the dipole−dipole term:

$$\frac{1}{T_{2Cs}}-\frac{1}{T_{1Cs}}=\frac{1}{5}\left(\frac{\mu_0}{4\pi}\right)^2\frac{\hbar^4\gamma_I^2\gamma_s^4B^2}{(3k_BT)^2r^6}J(J+1)\tau_{Cs} \quad (A12)$$

and we therefore assume that the terms for U^{4+} cannot be too different from those for the lanthanides.

Finally, the scalar relaxation term is described by

$$\frac{1}{T_{2sc}}-\frac{1}{T_{1sc}}=\frac{J(J+1)}{3}\left(\frac{A}{\hbar}\right)^2\left(\tau_{s1}-\frac{\tau_{s2}}{1+\omega_s^2\tau_{s2}^2}\right) \quad (A13)$$

where

$$\tau_{sj}^{-1}=k_{ex}+T_{je}^{-1} \quad (A14)$$

with $j = 1$ or 2. The only metal ion specific terms are J and $A/\hbar$. J is equal to 4, for both U^{4+} and Pr^{3+}, while $A/\hbar$ is twice as large as that for U^{4+}, as for the Pr^{3+}, which at 67.8 MHz corresponds to 4 Hz at 265 K and 0.5 Hz at 325 K.

The values of the neglected terms are field dependent, and higher by a factor of $(108.5/67.8)^2 = 2.56$ at 18.8 T as compared to 11.7 T. At the latter field, $(1/T_2 - 1/T_1)/P_M$ is typically 40000 Hz at 265 K and 1500 Hz at 325 K, at 18.8 T it ranges from 60000 to 2000 Hz between 270 and 325 K.

From this we conclude that, in the temperature region studied, the chemical exchange is the dominant term in the relaxation rate difference also for U^{4+}. We can test the assumptions above by comparing the quantity $(1/T_2 - 1/T_1)/P_M$ for the experimental data obtained at different temperatures at the three different magnetic fields used. The result is given in Supporting Information, Table S2.

The experimental results show that at temperatures above 300 K, there is a systematic change in the experimental ratio of $(1/T_2 - 1/T_1)/P_M$ from that calculated using the simplifications given above. The experimental data obtained at 400 MHz are much less precise than those obtained at 500 and 800 MHz. The data at temperatures below 305 K are in fair agreement with those obtained at higher field, but the data at higher temperatures are very uncertain. In view of this we have only used the experimental data for the 11.7 and 18.8 T data at temperatures below 305 K for the estimation of rate constants and activation parameters for the water exchange.

Supporting Information Available: Table S1, listing of primary ^{17}O NMR data as a function of temperature at two different magnetic fields, 11.7 and 18.8 T. Table S2, reduced relaxation rate differences at different magnetic fields. Table S3, spectroscopic and magnetic data used for relaxation rate estimates. Figure S showing the reduced chemical shifts for the U(IV) samples. This material is available free of charge via the Internet at http://pubs.acs.org.

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