An extreme water exchange rate: the europium(II) aqua ion

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The rate of water exchange at the europium(II) aqua ion is measured by a combined variable-temperature ^{17}O NMR and EPR study; it is the fastest aqua exchange rate ever directly measured by magnetic resonance for a non Jahn–Teller ion, 3.5×10^9 s^{-1} at 25 °C.

Water exchange on an aqua ion is one of the most fundamental chemical processes. An established field, water exchange rates have been measured on many of the aqua ions across the Periodic Table and span 20 orders of magnitude.[1] To date, no solvent exchange rates have been reported for the divalent lanthanides. The most easily accessible divalent lanthanide is europium(II). This report describes water exchange on $Eu^{2+}{}_{(aq)}$ as a function of temperature determined by a combined ^{17}O NMR and EPR study. Apart from its intrinsic interest, and to develop an understanding of ligand substitution kinetics at Eu^{II}, this work sheds light on two other areas. Europium(II) is very similar in size to Sr^{II} and exhibits a similar chemistry (excluding electron transfer).[2] Since water exchange on the heavier group 2 elements cannot be directly measured, Eu^{II} may provide insight as a spectroscopic probe in the chemistry of Ca^{II} and Sr^{II}.[3] Also, Eu^{II} is isoelectronic with Gd^{III}; we, and others, have extensively studied the factors influencing water exchange on Gd^{III} based contrast agents for magnetic resonance imaging (MRI).[4] Europium(II) being another f^7 ion allows us to further understand relaxation processes in ^8S ions.

The approach taken was the same as in our previous analyses† of Gd^{III} water exchange kinetics.[5] The source of Eu^{II} was the triflate salt, $Eu(O_3SCF_3)_2{\cdot}H_2O$.‡ From the measured relaxation rates and angular frequencies of $Eu^{2+}{}_{(aq)}$ solutions, $1/T_1$, $1/T_2$ and ω, and of a dilute triflic acid reference solution, $1/T_{1A}$, $1/T_{2A}$ and ω_A, the reduced relaxation rates and chemical shift $1/T_{1r}$, $1/T_{2r}$, and ω_r can be calculated, eqns. (1)–(3). Here,

$$\frac{1}{T_{1r}} = \frac{1}{P_m}\left[\frac{1}{T_1} - \frac{1}{T_{1A}}\right] = \frac{1}{T_{1m} + \tau_m} \tag{1}$$

$$\frac{1}{T_{2r}} = \frac{1}{P_m}\left[\frac{1}{T_2} - \frac{1}{T_{2A}}\right] = \frac{1}{\tau_m}\,\frac{T_{2m}^{-2} + \tau_m^{-1}T_{2m}^{-1} + \Delta\omega_m^2}{\left(\tau_m^{-1} + T_{2m}^{-1}\right)^2 + \Delta\omega_m^2} \tag{2}$$

$$\Delta\omega_r = \frac{1}{P_m}\left(\omega - \omega_A\right) = \frac{\Delta\omega_m}{\left(1 + \tau_m T_{2m}^{-1}\right)^2 + \tau_m^2\Delta\omega_m^2} \tag{3}$$

the subscript m refers to the relaxation rates of bound water and the chemical shift difference between bound and bulk water, P_m is the mole fraction of bound water, and $\tau_m = k_{ex}{}^{-1}$ is the residency time of a bound water molecule. The chemical shift of bound water is given by eqn. (4), where $A/\hbar$ is the

$$\Delta\omega_m = \frac{g_L\mu_B S(S+1)B}{3k_BT}\,\frac{A}{\hbar} \tag{4}$$

hyperfine coupling constant and the other symbols are constants.§ The longitudinal relaxation rate is dominated by the dipole–dipole and quadrupolar mechanisms, eqn. (5).

$$\frac{1}{T_{1m}} = \left[\frac{2}{5}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar^2\gamma_I^2\gamma_S^2}{r_{EuO}^6} S(S+1) + Q\right]\tau_R \tag{5}$$

The rotational correlation time is given by τ_R which has an exponential temperature dependence with an activation energy E_R, eqn. (6). The dipole–dipole mechanism is dependent on

$$\tau_R = \tau_R^{298} \exp\left[\frac{E_R}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \tag{6}$$

the Eu–O bond length ($r^6{}_{EuO}$) which we have set to 2.65 Å.[6] The reduced transverse relaxation rate allows the determination of the rate constant by eqn. (7), where $1/\tau_{1S} = k_{ex} + 1/T_{1e}$.

$$\frac{1}{T_{2sc}} = \frac{(A/\hbar)^2}{3} S(S+1)\tau_{1S} \tag{7}$$

The transverse electronic relaxation rates have been determined by EPR linewidth measurements, denoted Δ_{Hpp}. Eqns. (8) and (9) introduce three more parameters, Δ^2, the trace of the square

$$\begin{aligned}\frac{1}{T_{2e}} &= \frac{g_L\mu_B\pi\sqrt{3}}{h}\,\Delta H_{pp}\\ &= \Delta^2\tau_v\left[\frac{5.26}{1 + 0.372\omega_S^2\tau_v^2} + \frac{7.18}{1 + 1.24\omega_S\tau_v}\right]\end{aligned} \tag{8}$$

$$\tau_v = \tau_v^{298} \exp\left\{\frac{E_V}{R}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right\} \tag{9}$$

of the zero field splitting (ZFS) tensor τ_v, the correlation time modulation of the ZFS, and E_v, the activation energy defining the temperature dependence of τ_v. The longitudinal electronic relaxation rate can then be determined by the following relationship, eqn. (10). Finally, the temperature dependence

$$\frac{1}{T_{1e}} = \frac{1}{25}\Delta^2\tau_v\left\{4S(S+1) - 3\right\}\left(\frac{1}{1 + \omega_S^2\tau_v^2} + \frac{4}{1 + \omega_S^2\tau_v^2}\right) \tag{10}$$

of the exchange rate follows the Eyring equation (11). The

$$\begin{aligned}\frac{1}{\tau_m} = k_{ex} &= \frac{k_BT}{h}\exp\left\{\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right\}\\ &= \frac{k_{ex}^{298}T}{298.15}\exp\left\{\frac{\Delta H^\ddagger}{R}\left(\frac{1}{298.15} - \frac{1}{T}\right)\right\}\end{aligned} \tag{11}$$

reduced relaxation rates, reduced chemical shifts, and electronic transverse relaxation rates were fitted simultaneously as a function of temperature using eqns. (1)–(11). The fitted parameters are given in Table 1, and the fitted data shown in Fig. 1.

Table 1 Comparison of parameters for Gd^{III}[a] and Eu^{II} water exchange

Parameter	$[Eu(H_2O)_8]^{2+}$	$[Gd(H_2O)_8]^{3+}$
$10^{-9}\ k_{ex}^{298}/s^{-1}$	3.5 ± 0.4	0.80 ± 0.06
$\Delta H^{\ddagger}$/kJ mol^{-1}	18.2 ± 2	15.3 ± 1
$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	−0.2 ± 6	−23.1 ± 4
$10^{-6}\ (A/\hbar)$/rad s^{-1}	−3.70 ± 0.07	−5.3 ± 0.1
τ_R^{298}/ps	12 ± 1	41 ± 2
E_R/kJ mol^{-1}	18.2 ± 0.6	15.0 ± 1.3
τ_v^{298}/ps	0.4 ± 0.1	7.3 ± 0.5
E_v/kJ mol^{-1}	8.6 ± 0.8	18.4 ± 1.4
$10^{-20}\ \Delta^2$/ s^{-2}	5.4 ± 1.4	1.19 ± 0.09

[a] Ref. 4.

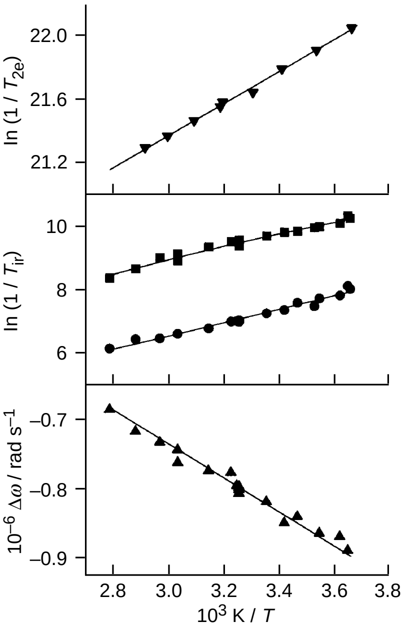

Fig. 1 Temperature dependence of the reduced ^{17}O chemical shifts (bottom), reduced ^{17}O longitudinal (circles) and transverse (squares) relaxation rates (middle), and of the transverse electronic relaxation rates (top)

As expected, the larger, less highly charged $[Eu(OH_2)_8]^{2+}$ ion undergoes water exchange faster than $[Gd(OH_2)_8]^{3+}$. The hyperfine coupling constant is lower for Eu^{II}, again, as expected since $A/\hbar$ is determined by the degree of interaction between the electron spin of the metal and the ^{17}O nucleus; the larger, less charged ion should interact less strongly with the oxygen donor atom. The rotational correlation time is very short for the Eu^{II} aqua ion. Although the precision associated with this number is very good, the actual error could be much larger since the measured T_1 of the sample was close to the T_1 of the reference (within 90%). Hence the rotational correlation time is based on the small difference between two large numbers, and τ_R should not be considered too meaningful. In contrast, the transverse relaxation rates provide a very good representation of the exchange rate. The value of $1/T_{2m}$ is dependent on contributions from electronic relaxation and chemical exchange. Since Eu^{II} has a longer electronic lifetime than Gd^{III} (shorter τ_v, larger Δ^2), the contribution of $1/T_{1e}$ to $1/T_{2m}$ is much less for the Eu^{II} aqua ion (only about 10%). The differences between measured T_2 values for Eu^{II} and reference are more than ten times greater than for the T_1 difference leading to increased accuracy.

The coordination number of the Eu^{II} aqua ion is not known. This report assumes a coordination number of eight based on analogy with Sr^{II}.[7] A coordination number of nine would lead to a value 8–9 times lower for k_{ex}^{298}, which is within the experimental error.

This report describes the second fastest water exchange rate ever measured [behind $Cu^{2+}{}_{(aq)}$] and its represents the fastest rate of water exchange measured on a non-Jahn–Teller ion.[8] Currently, this work is being expanded to examine the effects of magnetic field strength on both the NMR and EPR data, the effect of pressure on the rate of water exchange, and a molecular dynamics study on Eu^{II} solvation and water exchange.

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Footnotes and References

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† The equations listed are those used in the analysis and, in some cases, are simplified versions of the equations found in ref. 5. The simplifications are based on assumptions justified in ref. 5.

‡ $Eu(O_3SCF_3)_2$ was prepared by distilling degassed triflic acid onto $EuCO_3$[9] and then removing the water and excess triflic acid under reduced pressure. This process was repeated twice more, followed by drying at 90 °C *in vacuo* overnight to give $Eu(O_3SCF_3)_2{\cdot}H_2O$. Anal. Calc. for $C_2H_2EuF_2O_7S_2$: C, 5.13; H, 0.43; S, 13.70; F, 24.35. Found: C, 5.37; H, 0.46; S, 13.54; F, 23.91%. Solutions were prepared under nitrogen in a glove box by dissolving $Eu(O_3SCF_3)_2$ in water degassed by a triple freeze–pump–thaw cycle. Solutions were enriched with $H_2{}^{17}O$ labelled water. Solutions ranged from 0.02 to 0.15 mol kg^{-1} and enriched 3–6% in $H_2{}^{17}O$. Solution composition was checked by determination of total Eu content by titration with EDTA; the concentration agreed with that calculated from dissolution of solid $Eu(O_3SCF_3)_2$.

§ Constants: g_L = isotropic Landé factor, here 2.0; μ_B = Bohr magneton; B = magnetic field, 9.4 T; k_B = Boltzmann constant; γ_I = nuclear gyromagnetic ratio; γ_S = electron gyromagnetic ratio; $Q = (3\pi^2/10)\ \{(2I + 3)/[I^2(2I - 1)]\}\ \chi^2\ (1 + \eta^2/3)$; I = nuclear spin; χ = quadrupolar coupling constant; η = an asymmetry parameter; $\omega_S = \gamma_S B$. Values of the parameters are given in ref. 5.

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