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DMSO exchange on $[\text{Gd}(\text{DMSO})_8]^{3+}$ —a variable pressure ^{17}O NMR study

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Abstract

Variable temperature (at 9.4 and 14.1 T) and pressure (at 9.4 T) ^{17}O NMR relaxation and chemical shift experiments have been performed on DMSO solutions of $[\text{Gd}(\text{DMSO})_8]^{3+}$. It has been found that DMSO exchange is more than two orders of magnitude slower than water exchange ($k_{\text{ex}}^{298} = 6.2 \times 10^6 \text{ s}^{-1}$ for $[\text{Gd}(\text{DMSO})_8]^{3+}/8.3 \times 10^8 \text{ s}^{-1}$ for $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$). Comparison of activation volumes ($\Delta V^\ddagger = +8.2 \text{ cm}^3 \text{ s}^{-1}$ for $[\text{Gd}(\text{DMSO})_8]^{3+}/-3.3 \text{ cm}^3 \text{ s}^{-1}$ for $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$) shows that activation modes are different for solvent exchange on $[\text{Gd}(\text{DMSO})_8]^{3+}$ and $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$: DMSO exchange follows a dissociative activation mode in contrast to H_2O exchange which follows an associative activation mode. This change in activation mode is explained by the increase in molecular volume from H_2O to DMSO.

1. Introduction

The elucidation of solvent exchange reaction mechanisms is most effectively done by measuring the rate constant for the solvent exchange as a function of pressure [1]. It has been shown that the activation mode of the reaction can be directly linked to the activation volume, which is defined as the difference between the partial molar volume of the transition state and that of the reactants. Studies of solvent exchange mechanism on lanthanide ions concentrated up to now mainly on aqua ions [2] and water exchange on poly(amino carboxylate) complexes [3].

A variable temperature and pressure ^{17}O NMR study showed that water exchange on $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ is extremely rapid. An I_a reaction mechanism for water exchange was deduced from the negative activation volume $\Delta V^\ddagger = -3.3 \text{ cm}^3 \text{ mol}^{-1}$. Over the whole Ln^{3+} series

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eight- and nine-coordinated ions are close in energy. Nine coordination is favoured for the larger ions in the beginning and eight coordination for the smaller ions at the end of the series. The slightly less favoured state is similar in energy to the transition state/intermediate in an exchange process. The energy barrier is lowest in the middle of the series close to Sm^{3+} where an equilibrium between the two coordination states exists. Gadolinium is close to samarium in the lanthanide series and $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ has therefore the fastest water exchange rate measured on trivalent lanthanide ions.

In the last 15 years coordination properties of Gd^{3+} in solution have become of much interest due to its use as a paramagnetic centre in contrast agents for medical magnetic resonance imaging (MRI) [4]. The ^8S electronic state of Gd^{3+} is a key feature because it results in a relatively slow electron spin relaxation, T_{1e} . Water exchange on gadolinium (III) chelates with one H_2O molecule in the first coordination shell is about three orders of magnitude slower than on the aqua ion. This has been explained by a change of the activation mode from an associative one for $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ to a dissociative one for complexes of the form $[\text{GdL}(\text{H}_2\text{O})]^{n-}$ where L is DTPA^{5-} , DOTA^{4-} or another poly(amino carboxylate) ligand [5].

The only non-aqueous solvent where exchange rates have been measured over the Ln^{3+} series is DMF [6]. For the larger non-aqueous solvents such as DMF the equilibrium between nine and eight coordination is shifted towards larger ions in the beginning of the series (Ce^{3+} – Nd^{3+}). For the smaller lanthanides DMF exchange was measured, and a mechanistic crossover from I_d to D along the series Tb^{3+} to Yb^{3+} was attributed from positive activation volumes and from the rate laws [7, 8].

DMSO exchange on trivalent ions is studied for main group elements Al^{3+} and Ga^{3+} [9, 10]. Exchange rates on both ions are 4 (Al) and 200 (Ga) times slower than on the aqua complexes. The mechanisms of exchange processes on $[\text{M}(\text{DMSO})_6]^{3+}$ and on $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ ($\text{M} = \text{Al}, \text{Ga}$) are D [7]. We report here the first study of DMSO exchange on an eight-coordinated trivalent lanthanide ion.

2. Experimental details

All compounds and solutions were prepared, handled and stored in the dry nitrogen atmosphere of a glove-box to avoid water contamination (H_2O content: <5 ppm). $[\text{Gd}(\text{H}_2\text{O})_9](\text{OTf})_3$ ($\text{OTf}^- = \text{CF}_3\text{SO}_3^-$) was prepared as described in the literature [11]. Dimethyl sulphoxide, extra-dried over 4 Å molecular sieves, dimethylsulfoxide (DMSO) and anhydrous p.a. *n*-pentane were purchased from Acros and used as received. The Karl Fischer coulometric titration of DMSO gave a water content of 5 ppm. Triethyl orthoformate (TEOF) +99% was purchased from Acros and was degassed by a triple freeze–pump–thaw cycle and stored in the glove-box. All ^{17}O NMR measurements were performed with home-made enriched $(\text{CH}_3)_2\text{S}-^{17}\text{O}$ (1–2%). The metal content was determined by chelatometric titration with $\text{Na}_2\text{H}_2\text{EDTA}$ solution using xylenol orange indicator and urotropin for pH adjustment.

Synthesis of $[\text{Gd}(\text{DMSO})_8](\text{OTf})_3$. $[\text{Gd}(\text{H}_2\text{O})_9](\text{OTf})_3$ (1 g–1.33 mmol) was dissolved in triethyl orthoformate (4 g–27.0 mmol) and a few drops of ethanol were added to complete the dissolution. The solution was stirred at 50 °C for 45 min according to the method of Van Leeuwen and Groeneveld [12] and turned slowly from colourless to yellow. The solution was cooled at room temperature and DMSO (0.925 g–11.8 mmol) was added, leading to the immediate formation of a white solid. The precipitate was filtered, washed with TEOF, dried with *n*-pentane and pumped down to remove volatile impurities (yield 96%). Analysis calculated for $\text{C}_{19}\text{H}_{48}\text{O}_{17}\text{S}_{11}\text{F}_9\text{Gd}$: C, 18.56; H, 3.93; Gd, 12.79. Found: C, 18.68; H, 3.70; Gd, 12.80.

Synthesis of $(\text{CH}_3)_2\text{S}-^{17}\text{O}$. H_2 ^{17}O -labelled water (3.2 ml–140 mmol) in 13 ml of pyridine was added to a solution of dimethylsulfoxide (5.14 ml–70 mmol) in 50 ml of CH_2Cl_2 . A solution of Br_2 (4 ml–78 mmol) in 50 ml of CH_2Cl_2 was then added dropwise. After stirring for 30 min, anhydrous NaHSO_3 (1.4 g–14 mmol) was added to remove the excess of Br_2 and CH_2Cl_2 was evaporated (40 °C, ambient pressure). 50 ml of acetone were added to precipitate pyridinium bromide salt. The remaining solution was dried on anhydrous Na_2SO_4 and acetone was evaporated leading to the formation of yellow–brown oil. This oil was dissolved in 150 ml of benzene and the solution was filtered to remove insoluble impurities. Benzene was evaporated and the final product was refined by reduced pressure distillation (37 °C, 1.5 mbar) and stored under nitrogen over 4 Å molecular sieves (yield: 80%).

Variable temperature ^{17}O NMR measurements were performed at two magnetic fields using Bruker ARX-400 (9.4 T, 54.2 MHz) and Bruker Avance-600 (14.1 T, 81.1 MHz) spectrometers. The temperature was measured by replacing the sample with an NMR tube containing a Pt-100 resistance thermometer [13]. Solutions were introduced into spherical glass containers, fitting into ordinary 10 mm NMR tubes, in order to eliminate magnetic susceptibility corrections to chemical shifts [14].

Variable pressure ^{17}O NMR measurements were made on a Bruker ARX-400 spectrometer equipped with a previously described home-built probe head [15, 16]. The multinuclear probe (figure 1) fits into a normal bore NMR cryomagnet and is equipped with a receiver coil tunable for a large frequency band and with a second coil for ^1H decoupling and ^2H locking. The pressure range is from 0.1 to 200 MPa for liquid pressure. The temperature can be regulated between -50 and $+120$ °C by pumping a thermostated liquid through the helix on the high pressure vessel. The actual temperature is measured by a Pt-100 resistor implemented into the pressure vessel.

3. Results and discussion

Temperature dependences of the reduced transverse relaxation rates, $1/T_{2r}$, and chemical shifts, $\Delta\omega_r$, as calculated from measured ^{17}O NMR relaxation rates, $1/T_2$, and chemical shifts ω of the paramagnetic solutions and $1/T_{2A}$ and ω_A of a diamagnetic reference solution are shown in figure 2;

$$\frac{1}{T_{2r}} = \frac{1}{P_m} \left[\frac{1}{T_2} - \frac{1}{T_{2A}} \right]; \quad \Delta\omega_r = \frac{1}{P_m} (\omega - \omega_A); \quad P_m = \frac{q[\text{Ln}^{n+}]}{[\text{DMSO}]_{\text{tot}}}; \quad (1)$$

P_m is the mole fraction of DMSO molecules coordinated to the lanthanide ions and is proportional to the coordination number q . A theoretical description of $1/T_{2r}$ and $\Delta\omega_r$ is given by equations developed by Swift and Connick [17] and summarized for example by Caravan *et al* [18] and Tóth *et al* [5]. The temperature variation of the solvent exchange rate constant, k_{ex} , is obtained from a simultaneous fit of relaxation and shift data measured at two magnetic fields. It is assumed that k_{ex} obeys the Eyring equation:

$$k_{\text{ex}} = \frac{1}{\tau_m} = \frac{k_B T}{h} \exp \left\{ \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \right\} = \frac{k_{\text{ex}}^{298} T}{298.15} \exp \left\{ \frac{\Delta H^\ddagger}{R} \left(\frac{1}{298.15} - \frac{1}{T} \right) \right\}, \quad (2)$$

where ΔS^\ddagger and ΔH^\ddagger are the entropy and enthalpy of activation for the exchange process and k_{ex}^{298} is the exchange rate constant at 298 K.

Experimental $1/T_{2r}$ and $\Delta\omega_r$ values measured at two magnetic fields are shown in figure 2. A maximum of the transverse relaxation at temperatures of ~ 300 K is observed indicating a changeover from a fast to a slow exchange regime. This shows qualitatively that the DMSO exchange is much slower than water exchange where no such maximum is observed [19].

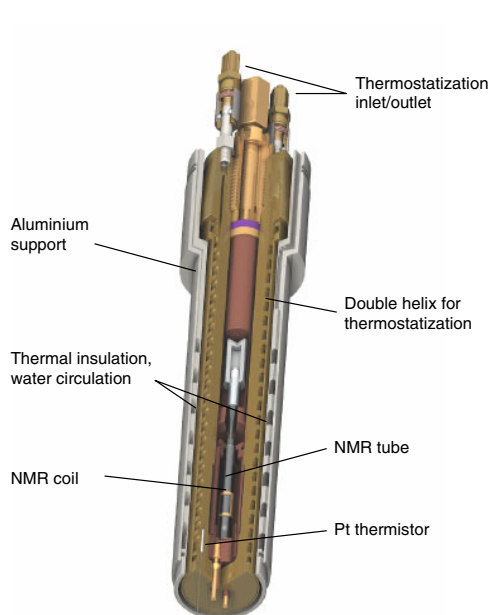


Figure 1. A high pressure, high resolution NMR probe for a 9.4 T normal bore NMR magnet; maximum working pressure 200 MPa, temperature range -50 to $+120$ °C. (This figure is in colour only in the electronic version)

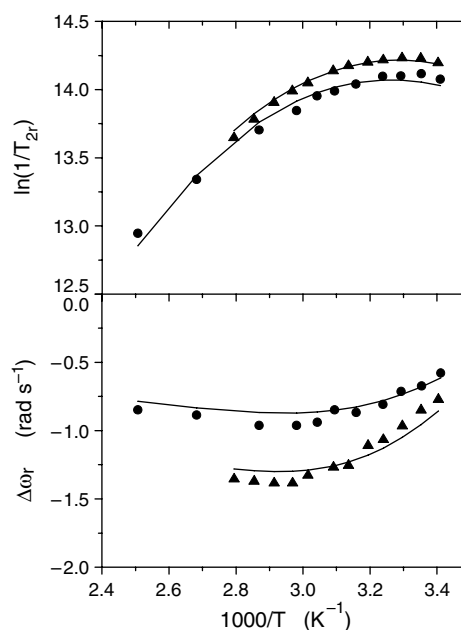


Figure 2. The temperature dependences at 9.4 T (54.2 MHz) (●) and 14.1 T (81.1 MHz) (▲) of reduced ^{17}O NMR transverse relaxation rates $1/T_{2r}$ and chemical shifts $\Delta\omega_r$ for $[\text{Gd}(\text{DMSO})_8]^{3+}$ ($[\text{Gd}^{3+}] = 4.558 \times 10^{-3} \text{ mol kg}^{-1}$).

Table 1. Rate constants and activation parameters for solvent exchange on Gd^{3+} .

	$[\text{Gd}(\text{DMSO})_8]^{3+}$ (this work)	$[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ [19]	$[\text{Tb}(\text{DMF})_8]^{3+}$ [6]	$[\text{Dy}(\text{DMF})_8]^{3+}$ [8]
k_{ex}^{298} (10^6 s^{-1})	6.2	800	19	6.3
ΔH^\ddagger (kJ mol^{-1})	32.8	15.3	14.1	13.8
ΔS^\ddagger ($\text{J mol}^{-1} \text{ K}^{-1}$)	-4.7	-23.1	-58	-69
ΔV^\ddagger ($\text{cm}^3 \text{ mol}^{-1}$)	+8.2	-3.3	+5.2	+6.1
Activation mechanism	I_d	I_a	I_d	I_d

Fitting of the equations [18] to the experimental data gives the exchange rate constant at 298 K, k_{ex}^{298} , and activation parameters ΔH^\ddagger and ΔS^\ddagger (table 1).

The pressure variation of the reduced transverse relaxation rates $1/T_{2r}$ is also calculated from equation (1). The experimentally measured pressure dependences of the bulk DMSO:

$$\frac{1}{T_{2A}} = \left(\frac{1}{T_{2A}} \right)_{P=0} \exp \left\{ \frac{-\Delta V_q^\ddagger}{RT} P \right\} \quad (3)$$

for relaxation rate $1/T_{2A}$ are shown in figure 3 for two temperatures. The fitted activation volumes (equation (3)) of the ^{17}O quadrupolar relaxation, ΔV_q^\ddagger , are $-9.7 \text{ cm}^3 \text{ mol}^{-1}$ (314.5 K) and $-8.5 \text{ cm}^3 \text{ mol}^{-1}$ (351.1 K). ΔV_q^\ddagger for ^{17}O relaxation for neat DMF was measured by Furrer [20]. He found ΔV_q^\ddagger at 298 K = $-7.4 \text{ cm}^3 \text{ mol}^{-1}$ with a strong temperature dependence. The quadrupolar relaxation rates, which are directly proportional to the rotational correlation times, τ_R , for rotation of the DMSO and DMF molecules, increase with pressure due to an

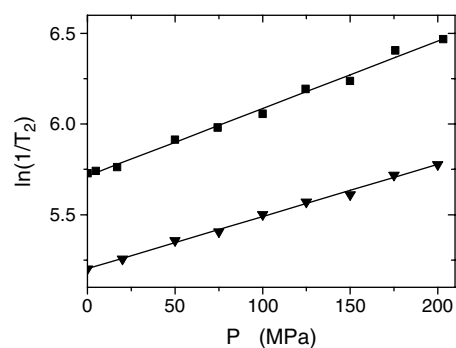


Figure 3. The pressure dependence at 9.4 T (54.2 MHz) of ^{17}O NMR transverse relaxation rates for neat DMSO at 351 K (■) and 314 K (▼).

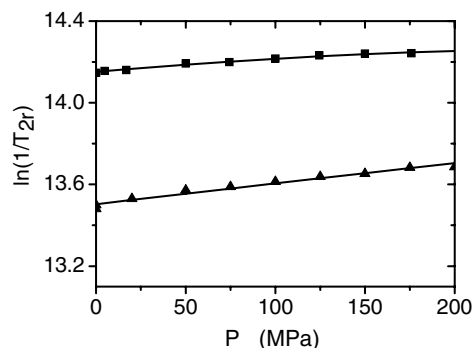


Figure 4. The pressure dependence at 9.4 T (54.2 MHz) of ^{17}O NMR reduced transverse relaxation rates for $[\text{Gd}(\text{DMSO})_8]^{3+}$ at 351 K (▲) ($[\text{Gd}^{3+}] = 6.089 \times 10^{-3} \text{ mol kg}^{-1}$), (■) 314 K ($[\text{Gd}^{3+}] = 5.526 \times 10^{-3} \text{ mol kg}^{-1}$).

increase in viscosity of the solution, as can be estimated from the Debye–Stokes equation,

$$\tau_{\text{R}} = \frac{4\pi\eta r_{\text{eff}}^3}{3k_{\text{B}}T} \quad (4)$$

where η is the viscosity and r_{eff} is an effective radius of the molecule.

Pressure variations of the reduced transverse relaxation rates $1/T_{2r}$ of Gd^{3+} in DMSO solutions are shown in figure 4. The pressure variation of the exchange rate constant k_{ex} is in general described by [7]

$$k_{\text{ex}} = \frac{1}{\tau_{\text{m}}} = (k_{\text{ex}})_{P=0} \exp\left\{-\frac{\Delta V^{\ddagger}}{RT}P\right\}. \quad (5)$$

The exchange rate constant at zero pressure is $(k_{\text{ex}})_{P=0}$ and the activation volume is ΔV^{\ddagger} . The activation volumes for solvent exchange are normally temperature independent and therefore the experimental data on $[\text{Gd}(\text{DMSO})_8]^{3+}$ has been fitted in a common non-linear regression leading to a single ΔV^{\ddagger} (table 1).

If solvent exchange of DMSO on $[\text{Gd}(\text{DMSO})_8]^{3+}$ is compared to that of $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$, it is found to be 130 times slower. This follows the general observation made on hexacoordinated metal ions [7]. For hard metal ions, oxygen bonded DMSO is a better ligand than water. No direct comparison can be made between the non-aqueous solvents DMSO and DMF because no exchange rates are measured for $[\text{Gd}(\text{DMF})_8]^{3+}$. We therefore compare the exchange rate measured for $[\text{Gd}(\text{DMSO})_8]^{3+}$ with those observed for the neighbouring lanthanide ions Tb^{3+} and Dy^{3+} : the rate constants at 298 K, k_{ex}^{298} , are of the same order of magnitude for both non-aqueous solvents (table 1). This observation shows that the very fast water exchange is really an exception due to the equilibrium between eight-coordinated and a small amount of nine-coordinated species in solution. The activation volumes for solvent exchange, determined from variable pressure experiments, show that the activation mode changes from an associative mode for H_2O as indicated by negative ΔV^{\ddagger} values to a dissociative one for DMSO with a positive ΔV^{\ddagger} (table 1). DMSO is normally considered as a better solvent than water. Therefore, the change in activation mode for the solvent exchange reaction is most probably due to the size of the solvent molecules: DMSO is considerable larger than H_2O and there is no space for a ninth solvent molecule to approach the $[\text{Gd}(\text{DMSO})_8]^{3+}$ complex. The activation volume for DMSO is slightly more positive than that measured for $[\text{Tb}(\text{DMF})_8]^{3+}$ and $[\text{Dy}(\text{DMF})_8]^{3+}$ [6]. An I_d mechanism is therefore assigned as the DMSO exchange on $[\text{Gd}(\text{DMF})_8]^{3+}$.

4. Conclusion

Variable magnetic field, temperature and pressure ^{17}O NMR relaxation and chemical shift experiments have been performed on DMSO solutions of $[\text{Gd}(\text{DMSO})_8]^{3+}$. It has been found that DMSO exchange on trivalent gadolinium is more than two orders of magnitude slower than water exchange. Comparison of the positive activation volume measured on $[\text{Gd}(\text{DMSO})_8]^{3+}$ with the negative one found for $[\text{Gd}(\text{H}_2\text{O})_8]^{3+}$ shows that activation modes for solvent exchange are different: DMSO exchange follows a dissociative activation mode in contrast to H_2O exchange which follows an associative activation mode. This change in activation mode is explained by the increase in molecular volume from H_2O to DMSO.

Acknowledgments

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