MAGNETIC RESONANCE IN CHEMISTRY, VOL. 35, 765–773 (1997)

Water Exchange on Magnesium(II) in Aqueous Solution: a Variable Temperature and Pressure ^{17}O NMR Study*

Anne Bleuzen, Pierre-André Pittet, Lothar Helm and André E. Merbach†
Institut de Chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie (BCH), CH-1015 Lausanne, Switzerland

Fast water exchange rate constants on diamagnetic metal ions can be measured using either a paramagnetic chemical shift agent or a paramagnetic relaxation agent. An approximate analytical equation was developed for the chemical shift agent method, valid in the limit of rapid exchange. The limits of validity of these methods are discussed. These were applied to the study of water exchange on $[Mg(H_2O)]_6^{2+}$ over a large temperature range (252–350 K) and up to a pressure of 200 MPa by ^{17}O NMR, leading to the following kinetic parameters: $k_{Mg}^{298} = 6.7 \pm 0.2 \times 10^5$ s^{-1}; $\Delta H_{Mg}^{\ddagger} = 49.1 \pm 0.7$ kJ mol^{-1}; $\Delta S_{Mg}^{\ddagger} = +31.1 \pm 2.2$ J K^{-1}; $\Delta V_{Mg}^{\ddagger} = +6.7 \pm 0.7$ cm^3 mol^{-1}. From these data, it is concluded that this process has an I_d mechanism with strong d character, without excluding a limiting D mechanism. © 1997 John Wiley & Sons, Ltd.

Magn. Reson. Chem. 35, 765–773 (1997) No. of Figures: 5 No. of Tables: 2 No. of References: 41

Keywords: NMR; ^{17}O NMR; Mg^{2+}; variable pressure; water exchange; solvation

Received 7 May 1997; accepted 12 June 1997

INTRODUCTION

In recent years, variable-temperature and variable-pressure oxygen-17 nuclear magnetic relaxation studies of water exchange on 2+ and 3+ ions in aqueous solution allowed the assignment of the mechanism for a variety of these reactions.[2] Very fast exchange reactions on paramagnetic cations could be studied because of strong interactions between unpaired electron spin and nuclear spin. Only a few diamagnetic cations could be studied directly by NMR. Because of the relatively slow water exchange rate ($k < 10^4$ s^{-1}) on these ions, direct observation of the bound water ^{17}O NMR resonance is possible for Ru(II),[3] RH(III),[4] Pd(II),[5] Ir(III)[6] and Pt(II).[7] For solutions of Be(II),[8] Al(III)[9] and Ga(III)[10] with a small chemical shift difference between the large free-water signal and the small bound-water signal, the former had to be broadened artificially by adding Mn^{2+}, a strong relaxation agent, to the solution. If the exchange rate from the bound-water site becomes too fast, the corresponding resonance line broadens strongly and finally disappears completely in the baseline. Another method to separate the free- and bound-water NMR signals is the addition of a chemical shift agent, normally Co^{2+} or a lanthanide ion. In this case the observation of the bound-water resonance is for the same reasons also restricted to slow exchange rates. If, however, the free-water signal is shifted very much from its normal resonance frequency by using a large concentration of shift agent and a very high magnetic field spectrometer, it should, in principle, also be broadened due to fast exchange between the diamagnetic bound site and the bulk water.

To test this approach, we measured water exchange rates on $[Mg(H_2O)_6]^{2+}$ using the relaxation agent and the chemical shift agent techniques mentioned above. A coordination number of 6 is well established for Mg^{2+} by proton NMR[11,12] and by x-ray diffraction.[13] A first study of water exchange on this ion was performed by Neely and Connick[14] using the relaxation agent technique and very high salt concentrations [*ca* 3.2 m $Mg(ClO_4)_2$ and 0.6 m $Mn(ClO_4)_2$] with a CW spectrometer at 1.4 T. A lifetime of about 2 μs at 25 °C was measured by ^{17}O NMR for this solution. In a recent classical molecular dynamics simulation study, Obst and Bradaczek[15] determined a mean residence time of 0.4 ns in a 1 ns MD simulation. Ligand substitution data for the substitution of H_2O on $[Mg(H_2O)_6]^{2+}$ are scarce: rates of *ca* 3×10^5 s^{-1} for the entry of divalent anions from the second coordination shell into the first shell have been obtained from ultrasonic absorption.[16,17]

EXPERIMENTAL

Materials and sample preparation

Magnesium perchlorate dihydrate (Fluka, puriss. p.a.), manganese perchlorate hexahydrate (Fluka, p.a.), 70%

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* High-Pressure NMR Kinetics, Part 83. For Part 82, see Ref. 1.

† Correspondence to: A. E. Merbach at Institut de Chimie Minérale et Analytique, Université de Lausanne, Bâtiment de Chimie (BCH), CH-1015 Lausanne, Switzerland.

Contact grant sponsor: Swiss National Science Foundation; Contract grant number: 20-45419.95.

CCC 0749–1581/97/110765–09 $17.50

perchloric acid (Merck, p.a.) and ^{17}O-enriched water (Yeda, 2 at.%) were used as received. For manganese-containing solutions, ^{17}O-enriched water (Yeda, 38.4 at.%, ^{1}H normalized) was distilled on a vacuum line. Terbium and lanthanum perchlorate salts were prepared and characterized as described previously.[18] ^{17}O-enriched nitromethane, prepared from about 5% ^{17}O-enriched silver nitrite as described previously,[19] was used as an internal reference for chemical shift measurements. Solutions were prepared by weight, their exact composition [given as moles of $M(ClO_4)_x$ per kg of solvent] and the sites populations of the water bound to terbium(III) [or manganese(II)] and magnesium(II) are given in Table 1.

Instrumentation and NMR measurements

Variable-temperature Fourier transform ^{17}O NMR spectra were obtained with Bruker AM-400 (9.4 T wide-bore magnet, 54.3 MHz, solutions containing manganese ions) and Bruker AMX-600 14.1 T normal-bore magnet, 81.3 MHz, solutions containing terbium ions) spectrometers using 10 mm broadband probes and working without lock. In order to minimize deformation of the resonance lines due to the very high magnetic susceptibility of the solutions containing high concentrations of terbium ions, we used spherical samples with these solutions.[20] Temperature was regulated with Bruker VT-2000 control units and measured by a substitution technique.[21] Sweep widths varied between 2.5 and 166 kHz depending on the observation frequency, signal width and experimental method (chemical shift, T_1 or T_2 measurement). The 90° pulse lengths were 16–21 μs for variable-temperature and 23 μs for variable-pressure measurements, and 1–4K data points were added depending on the sweep width used. Variable-pressure studies up to 200 MPa were performed on laboratory-built high-pressure probes for wide-bore (54.25 MHz)[22] and normal-bore high-field (81.3 MHz)[23] cryomagnets. Temperature was stabilized by pumping a thermostated liquid through the probe and measured with an accuracy of ± 0.5K (after all corrections) with a built-in Pt resistor. Longitudinal relaxation rates, $1/T_1$, were obtained by the inversion–recovery method[24] and transverse relaxation rates, $1/T_2$, were measured either by the Carr–Purcell–Meiboom–Gill[25] spin-echo technique or from linewidths by fitting a Lorentzian lineshape to experimental data.

Table 1. Compositions of aqueous solutions (*ca* 2% enriched in ^{17}O) used in the variable-temperature and variable-pressure ^{17}O NMR measurements

	$[Tb^{3+}]$		$[Mn^{2+}]$		$[Mg^{2+}]$	
Sample No.	m (mol kg^{-1})	P_m	m (mol kg^{-1})	P_m	m (mol kg^{-1})	P_m
1	0.199	0.029	—		—	
2	0.414	0.060	—		—	
3	0.172	0.025	—		—	
4	0.203	0.029	—		0.21	0.023
5	0.444	0.064	—		0.44	0.048
6	—		0.89	0.096	0.18	0.019
7	0.151	0.002			0.19	0.021
8[b]			0.64	0.07	3.52	0.38

[a] Sample Nos 1–5 and 7 contained 0.02 m CH_3NO_2 (*ca* 5% enriched in ^{17}O).
[b] Solution used by Neely and Connick[14]

The application of a chemical shift agent, $[Tb(H_2O)_8]^{3+}$ in our case, requires a very precise knowledge of the chemical shift of the coalesced ^{17}O water signal as a function of temperature. We used a small amount (*ca* 0.02 m) of ^{17}O-enriched CH_3NO_2 as an internal standard. Its chemical shift relative to water was measured at variable temperature and pressure using two samples with 0.2 mol of $[La(H_2O)_9](ClO_4)_3$ per kg of water and 0.1 m or 2.0 m of $HClO_4$. A chemical shift difference of 598 ppm between CH_3NO_2 and H_2O was observed, which is close to the literature value of 605 ppm.[26] To take into account the small temperature dependence, we used the linear expression $\delta = 612 - 424/T$, which was obtained by fitting. No pressure dependence of the chemical shift difference was observed up to 200 MPa. All chemical shift values given were measured relative to CH_3NO_2 by fitting Lorentzian lines to the signals and are reported relative to water using the linear expression mentioned above.

In the case of the relaxation agent method, a precise knowledge of the chemical shift is not necessary for the measurement of exchange rate constants. ^{17}O NMR spectra of sample No. 6 shows two signals separated by *ca* 320 ppm. The resonance at higher frequency was attributed to the ClO_4^- anion and that at lower frequency to the water molecules of $[Mg(H_2O)_6]^{2+}$. The chemical shift of water bound to Mg^{2+} is small, as expected. A precise measurement using this sample is not possible owing to the influence of the paramagnetic Mn^{2+} on the shift of ClO_4^-.

All non-linear least-squares fitting programs were written using MATLAB and its optimization toolbox running on a PC. A Levenberg–Marquard algorithm was used in all cases.

NMR DATA TREATMENT AND RESULTS

A direct study of fast solvent exchange on a diamagnetic cation is not possible owing to the small chemical shift and relaxation rate differences between bound and free solvent molecules. In order to increase these differences between the two sites, two methods are considered: the increase of the relaxation time difference between the sites by the use of a paramagnetic relaxation agent, or the increase of the chemical shift difference by the use of a paramagnetic chemical shift agent. In both cases, the water exchange on the paramagnetic agent must be must faster than the considered exchange on the diamagnetic site. The relaxing agent must produce a very short ^{17}O relaxation time of free water molecules; Mn^{2+} is an ideal example and has been used by Neely and Connick.[14] The shift agent must produce a large chemical shift of the free water molecules and small relaxation effect; Tb^{3+},[18] chosen for this study, meets these criteria. In both cases, the addition of the paramagnetic agent to the solution also means the addition of a third exchanging site. In our Mg^{2+} aqueous solutions, there are therefore three sites: bulk water (site A), water bound to the paramagnetic agent Mn^{2+} or Tb^{3+} (site B) and water bound to the diamagnetic Mg^{2+} cation (site C). From earlier results, it is evident that the exchange rate between water bound to the paramagnetic agent[18,27] (site B) and bulk water (site A) is much faster than the exchange rate between water bound to the diamagnetic cation[14] (site C) and bulk water.

Chemical exchange between three sites with a shift agent (fast exchange)

In our theoretical treatment we consider two approaches. The first consists in the use of the Kubo–Sack formalism,[28] which allows, in the absence of spin–spin coupling between the nuclei, a correct calculation of the NMR lineshape with chemical exchange between different sites. With a minimum of approximations this full treatment is applicable to both cases, the solutions containing the relaxation agent and the solutions with the shift agent. In our second approach, using some well justified approximations, we develop analytical expressions for the broadening of the coalesced NMR signal due to fast exchange between bulk water and the first coordination sphere of the two ions in solution.

First approach: Kubo–Sack formalism. NMR spectra resulting from solutions with three exchanging sites can be calculated using the Kubo–Sack formalism[28] with the 3×3 Kubo–Sack matrix, $\mathbf{K}$:

$$\mathbf{K} = \mathbf{D} + \mathbf{R}$$

$$\mathbf{D} = \begin{vmatrix} -i(\omega-\omega_A) - \frac{p_B}{p_A}k_B - \frac{p_C}{p_A}k_C & \frac{p_B}{p_A}k_B & \frac{p_C}{p_A}k_C \\ k_B & -i(\omega-\omega_B) - k_B & 0 \\ k_C & 0 & -i(\omega-\omega_C) - k_C \end{vmatrix} \qquad (1)$$

$$\mathbf{R} = \begin{vmatrix} -1/T_{2A} & 0 & 0 \\ 0 & -1/T_{2B} & 0 \\ 0 & 0 & -1/T_{2C} \end{vmatrix}$$

with $1/T_{2n} = \pi\Delta\nu_{1/2n}$, where n = A, B, C.

The three sites in our solutions are defined above. ω_n, p_n and $1/T_{2n}$ are the chemical shifts, the populations and the transverse relaxation rates of the three sites, respectively. k_B and k_C are the exchange rate constants for water exchanging from the first shells of Tb^{3+} and Mg^{2+}, respectively. A direct exchange of water molecules between the two bound sites was excluded in our treatment. In the case of fast exchange between the two bound sites and the bulk water site, only one NMR signal is observed at a chemical shift corresponding to the population weighted mean of the individual shifts [Eqn (2a)]:

$$\langle\omega\rangle = p_A\omega_A + p_B\omega_B + p_C\omega_C \qquad (2a)$$

$$\left\langle\frac{1}{T_2}\right\rangle = p_A\frac{1}{T_{2A}} + p_B\frac{1}{T_{2B}} + p_C\frac{1}{T_{2C}} \qquad (2b)$$

$$\left\langle\frac{1}{T_1}\right\rangle = p_A\frac{1}{T_{1A}} + p_B\frac{1}{T_{1B}} + p_C\frac{1}{T_{1C}} \qquad (2c)$$

The transverse relaxation rate (which is linked to the width of the resonance line) contains contributions originating from the individual relaxation rates $1/T_{2n}$, of the three sites A, B and C and from the exchange processes. The relaxation rates of the coalesced signal without exchange contribution are given by $\langle 1/T_2\rangle$ [Eqn (2b)] and $\langle 1/T_1\rangle$ [Eqn (2c)]. In our case, $\langle 1/T_2\rangle$ can be approximated by the longitudinal relaxation rate, $\langle 1/T_1\rangle$, which, in the case of fast exchange, can be determined experimentally from the coalesced NMR signal. This approximation can be justified by two reasons: first, in the case of ^{17}O NMR in diamagnetic solutions the quadrupolar relaxation mechanism is dominant, and therefore in the extreme narrowing condition $1/T_{2n} = 1/T_{1n}$ (n = A, B, C); second, it has been shown that for water in the first coordination shell of paramagnetic lanthanide ions such as Tb^{3+}, $1/T_{1B}$ and $1/T_{2B}$ are equal, within experimental error.[18] The relaxation excess of the coalesced resonance due to chemical exchange can therefore be obtained experimentally from the difference between transverse and longitudinal relaxation rates, $1/T_2$–$1/T_1$ (in doing so, we assume that the observed transverse relaxation rate, $1/T_2$, is equal to the summation of the non-exchange contribution, $\langle 1/T_2\rangle$, and the exchange contribution: this assumption is strictly valid in the fast exchange regime and has been verified numerically over the temperature range studied). Because no experimental results for individual relaxation rates $1/T_{2B}$ and $1/T_{2C}$ can be obtained, we used the Kubo–Sack formalism to calculate only the broadening of the coalesced resonance due to exchange. This was established by setting the relaxation contribution (matrix $\mathbf{R}$) to the Kubo–Sack matrix ($\mathbf{K}$) equal to zero [Eqn (1)]. With this approximated matrix, we calculated numerically the lineshapes $V(\omega)$ of the spectra:[29]

$$V(\omega) = Re(C\mathbf{P}\mathbf{K}^{-1}\mathbf{I})$$

$$\mathbf{P} = |p_A \quad p_B \quad p_C| \qquad (3)$$

where $\mathbf{I}$ = unity vector and C = constant. The resonance frequency of this single resonance spectrum, corresponding to $\langle\omega\rangle$, and its linewidth, corresponding to the exchange broadening, were obtained by fitting a Lorentzian line to $V(\omega)$.

Second approach: approximate analytical expressions. Equations describing chemical shift and relaxation time behavior as a function of exchange rate are well known.[30] In the case of an exchange between two sites, normally named 'bound' for water molecules in the first coordination sphere of cations and 'free' for bulk water molecules, analytical expressions exist for $1/T_1$, the measured longitudinal relaxation rate, $1/T_2$, the measured transverse relaxation rate, and $\Delta\omega$, the observed resonance frequency minus that of pure water.[31] For an exchange between a site with a low concentration of bound water molecules and the bulk of the solution, Swift and Connick[32,33] developed approximate equations:

$$\frac{1}{T_2} = \frac{1}{T_{2A}} + p_B k_B \frac{(T_{2B}^{-1} + k_B)T_{2B}^{-1} + \Delta\omega_B{}^2}{(k_B + T_{2B}^{-1})^2 + \Delta\omega_B{}^2} \tag{4}$$

$$\Delta\omega = p_B \frac{k_B{}^2\,\Delta\omega_B}{(k_B + T_{2B}^{-1})^2 + \Delta\omega_B{}^2} \tag{5}$$

$\Delta\omega_B$ is the chemical shift difference between the bound site (ω_B) and the bulk water signal (ω_A) in absence of exchange [Fig. 1(a)]. In a similar way one obtains for longitudinal relaxation[33,34]

$$\frac{1}{T_1} = \frac{1}{T_{1A}} + p_B \frac{1}{k_B^{-1} + T_{1B}} \tag{6}$$

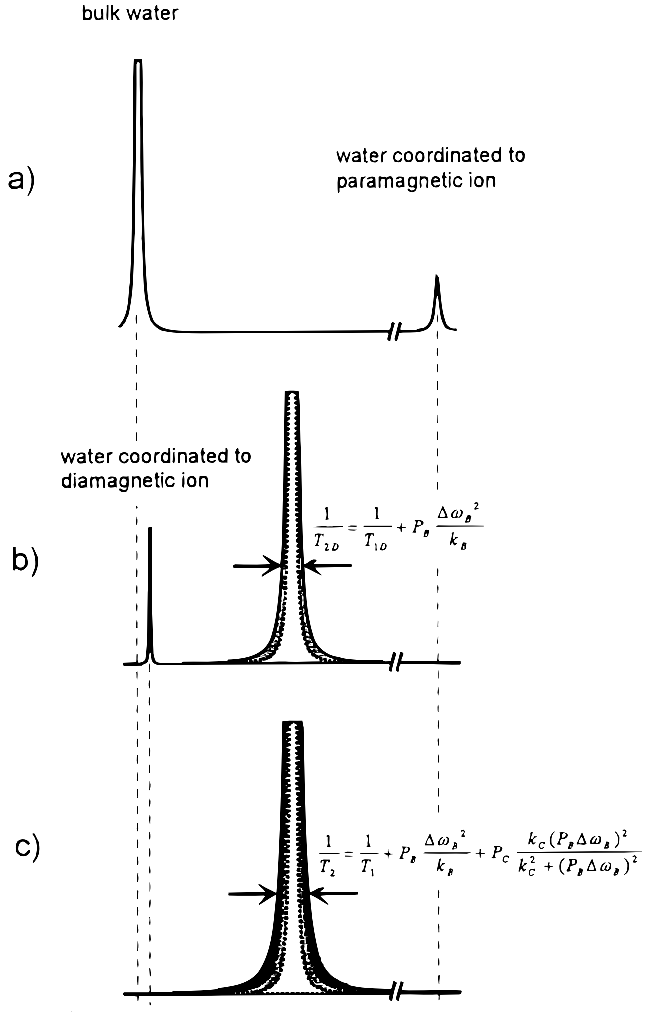

Figure 1. Schematic representation of NMR spectra with three-site exchange. (a) Spectrum without exchange (diamagnetic peak hidden under the bulk water peak); (b) fast exchange between water coordinated to the paramagnetic ion and no exchange with water coordinated to the diamagnetic ion; (c) both exchange processes are in the fast exchange limit.

In general, if there are more than two exchanging sites, no simple analytical solutions of the modified Bloch equations for the relaxation rates and for the chemical shifts exist.[35] The very fast exchange between the paramagnetic site and bulk water enables then both to be treated as a single site (site D). Thus our three-site system can be well described by a two-site exchange between a 'paramagnetic solvent' (site D) and water molecules bound to the diamagnetic Mg^{2+} cation (site C). In Eqns (4) and (6), the relaxation rates of bulk water have then to be replaced by $1/T_{2D}$ and $1/T_{1D}$, the relaxation rates of the 'paramagnetic solvent.' As has been shown before, $1/T_{1B} \approx 1/T_{2B}$ and therefore the difference between the transverse and longitudinal relaxation rates to a good approximation[18] given by

$$\frac{1}{T_{2D}} - \frac{1}{T_{1D}} = p_B \frac{\Delta\omega_B{}^2}{k_B} \tag{7}$$

The chemical shift difference, $\Delta\omega_D$, between the resonance of water molecules bound to the diamagnetic cation (ω_C) and the coalesced signal of the 'paramagnetic solvent' ($p_B\,\Delta\omega_B$) is to a good approximation given by Eqn (8) because the chemical shift of water bound to first- and second-row diamagnetic ions is normal small (a few ppm).[8–10]

$$\Delta\omega_D = -p_B\,\Delta\omega_B = \Delta\omega \tag{8}$$

For water bound to diamagnetic metal ions, $(1/T_{2Q})^{298}$ is smaller than 10^3 s^{-1} (Be^{2+} 739 s^{-1};[8] Ru^{2+} 378 s^{-1};[3] Pd^{2+}: 465 s^{-1};[5] Pt^{2+} 455 s^{-1} [7]). We can therefore assume that $k_C \gg 1/T_{2C}$ and with $T_{1C} = T_{2C}$ (see above) the difference between the experimental transverse and longitudinal relaxation rates is given for our three-site exchange by

$$\frac{1}{T_2} - \frac{1}{T_1} = p_B\left(\frac{\Delta\omega_B{}^2}{k_B}\right) + p_C \frac{k_C(p_B\,\Delta\omega_B)^2}{k_C{}^2 + (p_B\,\Delta\omega_B)^2} \tag{9}$$

The right-hand side of Eqn (9) is divided into two terms. The first corresponds to the broadening of the free-water signal by the fast exchange of water molecules of the paramagnetic agent [Fig. 1(b)] and the second corresponds to the broadening of the signal of the 'paramagnetic solvent' (site D) by the fast exchange of water from the diamagnetic cation [Fig. 1(c)]. It is evident that a precise measurement of k_C depends strongly on the knowledge of the exchange rate (k_B) and the chemical shift ($\Delta\omega_B$) of water bound to the lanthanide ion, used as a shift agent.

Chemical exchange between three sites with a relaxation agent (slow exchange)

Although the solutions with relaxation agent can theoretically be treated using the full Kubo–Sack formalism, an approximation by a two-site exchange is straightforward. The transverse relaxation of the 'paramagnetic solvent' [site D, which is the fast exchange between the paramagnetic relaxation agent (site B) and bulk water site A)] is very fast and therefore the mathematical condition for slow exchange is fulfilled: $k_C \ll |1/T_{2C} - 1/T_{2D}|$.[33] The strong broadening of the signal of the 'paramagnetic solvent' allows a direct observation of the signal of water bound to magnesium, as long as the exchange on this ion does not lead to an extremely large signal:[14,33]

$$\frac{1}{T_2} = \pi(\Delta\nu_{1/2}) = k_C + \frac{1}{T_{2C}} \approx k_C \qquad (10)$$

Because the exchange rate, k_C, is much faster than the quadrupolar relaxation $1/T_{2C}$, the linewidth $\Delta\nu_{1/2}$ measures directly the exchange rate constant.

Temperature dependence of water exchange on $Mg(H_2O)_6^{2+}$

We measured the temperature dependence of the transverse and longitudinal relaxation rates and the chemical shifts of samples containing solutions with different concentrations of $Tb(ClO_4)_3$ only and of $Tb(ClO_4)_3$–$Mg(ClO_4)_2$ mixtures (Table 1). Furthermore, at very low temperature we measured directly the ^{17}O NMR linewidth of the resonance of water bound to Mg^{2+} using high concentrations of Mn^{2+} as a relaxation agent (sample No. 6, Table 1).

The temperature dependence of the exchange rate constant is given by Eyring's equation:

$$k(T) = \frac{k_B T}{h}\exp\left(\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right)$$

$$= k^{298}\,\frac{T}{298.15}\exp\left[\frac{\Delta H^\ddagger}{R}\left(\frac{1}{298.15} + \frac{1}{T}\right)\right] \qquad (11)$$

where $\Delta S^\ddagger$ and $\Delta H^\ddagger$ are the entropy and the enthalpy of activation, respectively, and k^{298} is the exchange rate constant at 298 K. The chemical shift of water bound to Tb^{3+} is given by[18]

$$\Delta\omega_B = \frac{g_L(g_L - 1)J(J+1)\mu_B B}{3k_B T}\,\frac{A}{\hbar} \qquad (12)$$

where g_L is the isotropic Landé factor ($g_L = 1.5$ for Tb^{3+}), J is the electron spin angular momentum quantum number ($J = 6$ for Tb^{3+}), $A/\hbar$ is the hyperfine coupling constant, μ_B is the Bohr magneton, and B the static magnetic field. The parameters $\Delta H^\ddagger_{Mg}$, $\Delta S^\ddagger_{Mg}$ (or k^{298}_{Mg}), $\Delta H^\ddagger_{Tb}$, $\Delta S^\ddagger_{Tb}$ (or k^{298}_{Tb}) and $A/\hbar$ were obtained from a non-linear least-squares fit of the exchange broadening and the chemical shift to experimental $1/T_2 - 1/T_1$ and $\Delta\omega$ values measured with samples 1, 2, 4 and 5 (i.e. Tb^{3+} in the presence and absence of Mg^{2+}). Simultaneously, exchange rate constants from solutions with relaxation agent [sample 6, Eqn (10)] were fitted to the experimental data. The experimental data, as well as the calculated curves resulting from the fit (full lines), are shown in Fig. 2 and the fitted parameters are given in Table 2.

These parameters were then introduced into the approximate analytical expressions [Eqns (7)–(9)] and the calculated curves (as a function of 1000/T) are represented in Fig. 2 as short-dashed lines. The very good agreement between curves obtained from our approximate treatment and the Kubo–Sack formalism justifies the approximations used in our equations. At low temperatures ($T < 280$ K) the approximate equation for the chemical shift [Eqn (8)] no longer describes the experimental data correctly. This failure arises because the fast exchange limit is no longer valid for the exchange process between the 'paramagnetic solvent' and water bound to Mg^{2+}.

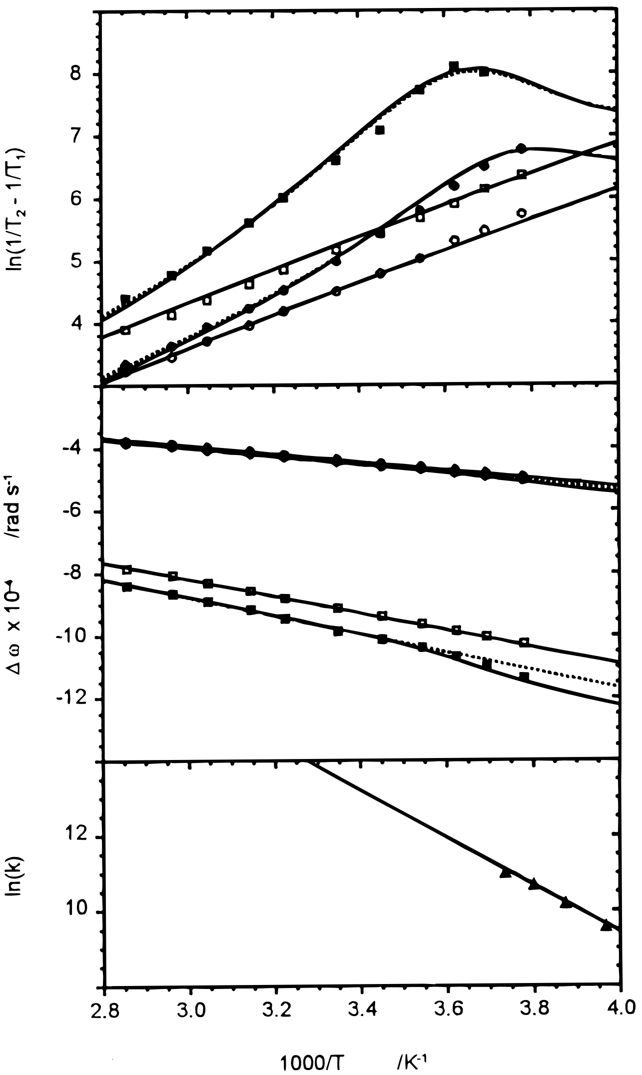

Figure 2. Variable-temperature ^{17}O NMR results ($B_0 = 14.1$ T) for sample Nos (○) 1, (□) 2, (●) 4, (■) 5 and (▲) 6. Full lines result from simultaneous non-linear least-squares fitting using Kubo–Sack formalism. Short-dashed lines were calculated by the approximate analytical method using parameters from the fit.

Table 2. Parameters obtained from least-squares fits of the variable-temperature and variable-pressure ^{17}O NMR measurements

Parameter	This work	Neely and Connick[14]
k^{298}_{Mg} ($\times 10^5$ s^{-1})	6.7 ± 0.2	5.3 ± 0.3
$\Delta H^\ddagger_{Mg}$ (kJ mol^{-1})	49.1 ± 0.7	43
$\Delta S^\ddagger_{Mg}$ (J K^{-1} mol^{-1})	+31.1 ± 2.2	+8
k^{298}_{Tb} ($\times 10^8$ s^{-1})	7.3 ± 0.1	
$\Delta H^\ddagger_{Tb}$ (kJ mol^{-1})	14.3 ± 0.4	
$A/\hbar$ ($\times 10^6$ s^{-1})	−4.588 ± 0.007	
$\Delta V^\ddagger_{Mg}$ (cm^3 mol^{-1})	+6.7 ± 0.7	
$\Delta\beta^\ddagger_{Mg}$ (cm^3 mol^{-1} MPa^{-1})	+1.4 ± 0.7	
$\Delta V^\ddagger_{Tb}$ (cm^3 mol^{-1})	−5.1 ± 0.5	
$\Delta\beta^\ddagger_{T\beta}$ (cm^3 mol^{-1} MPa^{-1})	−0.7 ± 0.5	
P_1 (MPa^{-1})	−0.9 ± 0.6	

Pressure dependence of water exchange on $Mg(H_2O)_6^{2+}$

Oxygen-17 NMR studies were performed as a function pressure up to 200 MPa. The pressure dependence of ln k is given by the quadratic equation

$$(\ln k)_P = \ln k_0 - \frac{\Delta V_0^{\ddagger}}{RT} P + \frac{\Delta\beta^{\ddagger}}{2RT} P^2 \qquad (13)$$

where k_0 is the exchange rate and $\Delta V_0^{\ddagger}$ is the activation volume, both at zero pressure, and $\Delta\beta^{\ddagger}$ is the compressibility coefficient of activation.[36] The pressure dependence of $\Delta\omega_B$ is expected to be small and can be described by a linear relationship:

$$\Delta\omega_B = p_B \Delta\omega_{(P=0)}(1 + P_1 P) \qquad (14)$$

where P_1 is a proportionality factor. This approach has already be used to determine very fast water exchange kinetics on trivalent lanthanide ions.[38,39] The variable pressures measurements were performed using both the chemical shift (at $T = 286.0$ K, sample Nos 3 and 7) and relaxation technique (at $T = 261.2$ K, sample No. 6) described above. The activation volume for water exchange on Tb^{3+} (sample No. 3) was obtained by fitting Eqns (7), (13) and (14) to the experimental data points [Fig. 3(a) and Table 2].

Because of the very good agreement between the full Kubo–Sack formalism and the simplified analytical treatment, only the later one has been used to evaluate the experimental data with shift agent. Rate constants as a function of pressure for water exchange on Mg^{2+} can be calculated from experimental $1/T_2 - 1/T_1$ data using the equation

$$k_C = \frac{\Delta\omega_C^2 \pm \sqrt{\Delta\omega_C^4 - 4(A - B)^2\, \Delta\omega_C^2}}{2(A - B)}$$

with

$$A = \frac{1}{p_C}\left(\frac{1}{T_2} - \frac{1}{T_1}\right); \quad B = \frac{p_B}{p_C}\frac{\Delta\omega_C^2}{k_B} \qquad (15)$$

This equation is obtained from Eqn (9) by simple algebraic transformation. The negative sign in Eqn (15) leads to very small exchange rates, which is in contradiction to the assumption of moderately fast exchange on these ions. Pressure variations of k_B and $\Delta\omega_B$ were introduced using the parameters obtained from solutions containing only Tb^{3+} ions (Table 2). Pressure-dependent exchange rates k_C for the relaxation agent solutions where obtained directly from the experiment [Eqn (10)].

Activation volumes for water exchange on Mg^{2+} were calculated by fitting Eqn (13) to the exchange rate constants k_C. Although the two series of experimental k_C values were measured at different temperatures the pressure dependence as described by $\Delta V_0^{\ddagger}$ and $\Delta\beta^{\ddagger}$ is the same. The very good agreement between data points obtained with chemical shift and relaxation agents is shown in Fig. 3 (bottom).

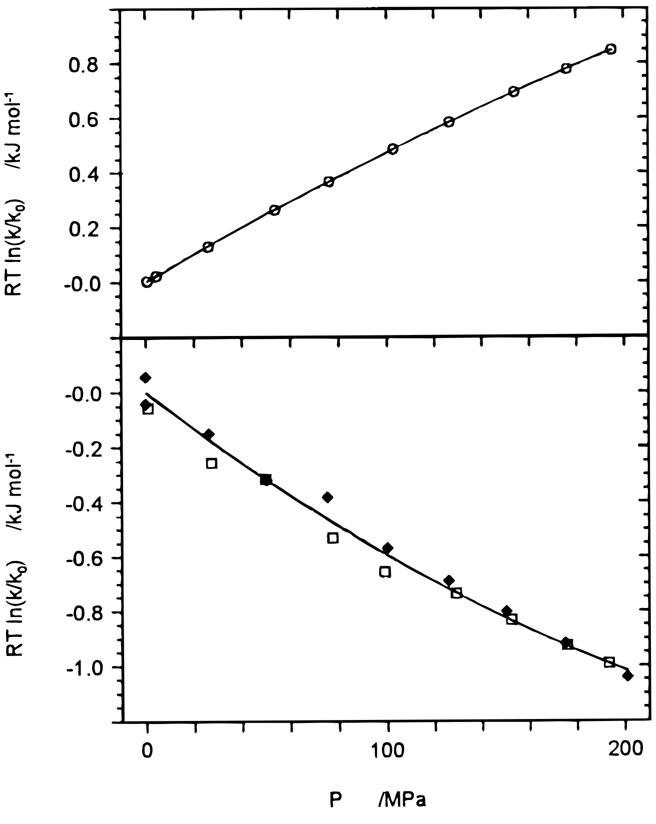

Figure 3. Pressure variation of water exchange rates calculated from variable-pressure ^{17}O NMR results for $[Tb(H_2O)_8]^{3+}$ at 286.0 K (○, sample 3, 14.1 T) and $[Mg(H_2O)_6]^{2+}$ at 261.2 K (◆, sample 6, 9.4 T, relaxation agent) and 286.0 K (□, sample 7, 14.1 T, chemical shift agent). Lines correspond to simultaneous non-linear least-squares fitting.

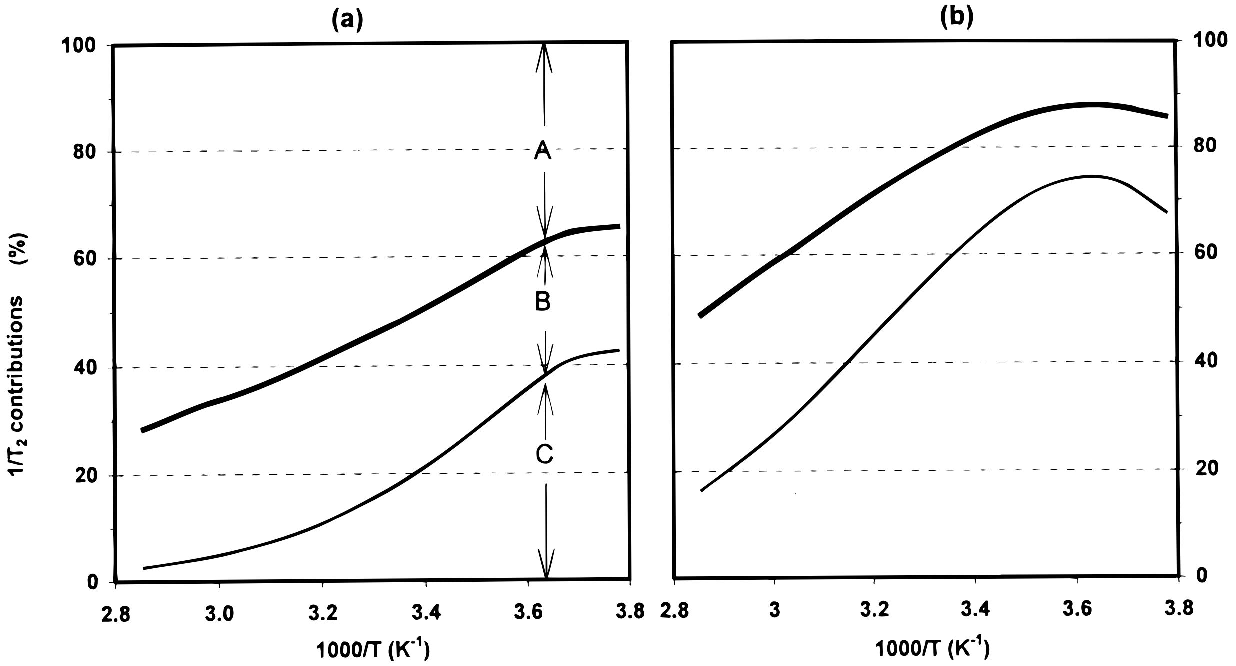

Figure 4. Temperature dependence of the three contribution in Eqn (9) for (a) sample 4 and (b) sample 5. The contributions are (A) $1/T_1$, B) $p_B(\Delta\omega_B^2/k_B)$ and (c) $p_C[k_C(p_B\Delta\omega_B)^2/k_C^2 + (p_B\Delta\omega_B)^2]$.

DISCUSSION

Evaluation of the experimental methods and data treatment

Before comparing the method using chemical shift agents with that using relaxation agents, we first want to discuss the validity of the approximate analytical expression versus the Kubo–Sack formalism. Within this last formalism we assume first the additivity of the non-exchange contribution, $\langle 1/T_2 \rangle$, and of the exchange contribution, and second we replace $\langle 1/T_2 \rangle$ by $\langle 1/T_1 \rangle$, which is experimentally measurable. Both assumptions are verified in the fast exchange regime. The good quality of the approximation using the analytical expression has already been shown in Fig. 2. Besides the much smaller computing effort, the approximate analytical expression has the advantage of showing in a clear manner the contribution to the relaxation rate due to the water exchange on the diamagnetic ion. Figure 4 gives plots for the contributions (in %) of mean relaxation ($\langle 1/T_1 \rangle$) (A), of exchange from Tb^{3+} coordination sphere (B) and of exchange from the Mg^{2+} coordination sphere (C) as a function of inverse temperature. These curves show that the contribution of the exchange on the diamagnetic cation to the total line broadening varies from about 5 to 75% on the temperature range. Furthermore, the contribution weights depend on the concentrations of the species. The contribution due to the exchange from the diamagnetic ion increases with increasing salt concentrations. Increasing the concentration of the paramagnetic ion too much leads to very short T_1 and T_2 relaxation times which are difficult to measure accurately.

Once the validity of the simplified treatment has been checked, the analytical expressions of the exchange rate constants [Eqn (15)] can be used to calculate k_C and to compare exchange rates obtained by the chemical shift and by the relaxation agent method directly. Figure 5 shows exchange rates as obtained with both techniques together with old data from Neely and Connick.[14] Experimental exchange rates are now available over a wide temperature range (253–350 K) which allows more precise fitting of activation enthalpy and entropy. Figure 5 furthermore shows the good quality of the old data obtained with very high concentrations at low magnetic field.

The advantage of the relaxation agent method is the direct observation of the NMR signal of bound water molecules which leads to a direct measurement of the exchange rate constant. It is obvious that this method is limited to relatively slow exchange because the signals of the water bound to the diamagnetic cation become very large with the increase in the exchange rates. Furthermore, high concentrations of paramagnetic and dia-

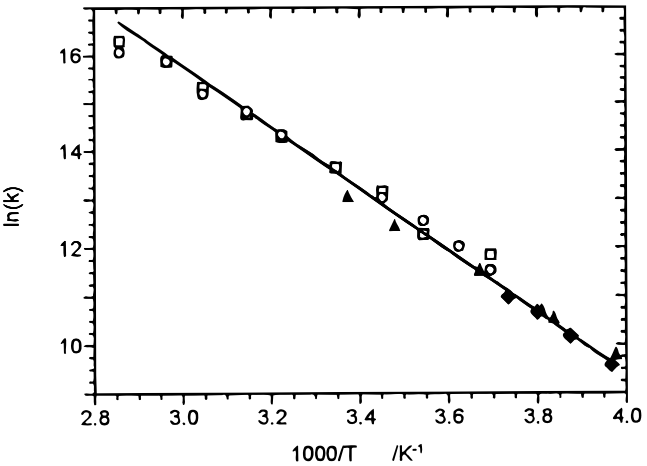

Figure 5. Temperature variation of water exchange rates obtained from different samples, (○) No. 4, (□) No. 5 and (◆) No. 6, and (▲) from Neely and Connick's data.[14]

magnetic salts and a high enrichment of oxygen-17 have to be used to obtain NMR spectra of reasonable quality in a reasonable time. Using Gd^{3+} as relaxation agent instead of Mn^{2+} would, owing to stronger relaxation enhancement of gadolinium(III), allow lower concentrations of the relaxation agent, but owing to the higher charge of Gd^{3+} would lead to similar ionic strength.

The method based on a strong chemical shift agent is less direct; it involves two solutions, one with and one without the diamagnetic ions. Furthermore, the kinetic data are obtained from the difference in transverse and longitudinal relaxation rates which may be close in the case of very fast exchanges. Good results imply a precise knowledge of concentrations of the paramagnetic ion in both solutions. On the other hand, accurate relaxation rates can be obtained even with low ^{17}O water enrichment thanks to the high concentration (55 mol kg^{-1}) of the measured water signal. This shift agent method extends considerably the measurable rate contant for water exchange on diamagnetic cations up to 10^7 s^{-1} (for comparison, this would correspond to a linewidth of 3 MHz for the relaxation agent method!).

Water exchange on $[Mg(H_2O)_6]^{2+}$

Magnesium(II) is an important metal ion in biology; however, it has received less attention than transition metals because the latter are more readily studied by common spectroscopic and electrochemical methods. The water exchange rate of 7.4×10^5 s^{-1} (at 298 K) measured on $Mg(H_2O)^{62+}$ ions is only the second one directly determined on divalent main group ions, besides $Be(H_2O)_4^{2+}$, and it is the first one of a hexacoordinated ion of this group. This value is close to the values of k_{34} ranging from 2.8×10^5 to 3.0×10^5 s^{-1} obtained at 20 °C by ultrasonic absorption for the third step of the Eigen–Tamm mechanism for water substitution on $[Mg(H_2O)_6]^{2+}$ by SO_4^{2-}, CrO_4^{2-} and $S_2O_3^{2-}$ ions.[16,17] This third step corresponds to the rate of replacement of an inner-sphere water molecule by an anion sitting in the second coordination sphere of the hexaaquaion. The water exchange rate for Mg^{2+} lies between those of Co^{2+} ($k^{298} = 3.18 \times 10^6$ s^{-1})[40] and Ni^{2+}($k^{298} = 3.15 \times 10^4$ s^{-1})[36] and reflects the order of ionic radii of these three ions ($Co^{2+} = 74$ pm, $Mg^{2+} = 72$ pm, $Ni^{2+} = 69$ pm,).[41] The activation volume of $+6.7$ cm^3 mol^{-1} is strongly positive and also intermediate to those obtained for Co^{2+} ($+6.1$ cm^3 mol^{-1}) and Ni^{2+} ($+7.1$ cm^3 mol^{-1}).[40] For Ni^{2+}, with the most positive $\Delta V^\ddagger$ value so far observed for a divalent aquaion, a dissociative interchange mechanism, I_d, has been assigned for the water exchange reaction.[40] For Mg^{2+} we conclude to the same mechanism according to the following two arguments. First the activation volumes for the two metal ions are very similar and second the fact that the rate of complex formation is close to the water exchange rate is indicative of metal–water bond rupture as the rate-determining step. Recently, Rotzinger[42] concluded from *ab initio* calculations on some clusters of transition metal ions that the energies of five-coordinated intermediates of Ni^{2+} are close to their respective transition states. This means that the mechanism for water exchange for this cation is close to a dissociative mechanism. We therefore cannot exclude that in the case of Mg^{2+} a limiting dissociative mechanism (D) is operating.

Supplementary material

Variable temperature and pressure relaxation rates and chemical shifts and the MATLAB program used for calculation of lineshapes are available from A.E.M.

Acknowledgements

We thank Dr Urban Frey for technical help with the 14.1 T high-pressure NMR probe. This work was financially supported by the Swiss National Science Foundation (Grant No. 20-45419.95).

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