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^{1}H NMRD Studies of Solutions of Paramagnetic Metal Ions in Ethyleneglycol

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Abstract

Solvent ^{1}H T_1^{-1} values at magnetic fields between 2.3 × 10^{-4} and 1.2 T were measured for ethyleneglycol solutions of manganese(II), cobalt(II), nickel(II), copper(II), and gadolinium(III) salts in the temperature range −10–+40 °C. The T_1^{-1} profiles were interpreted on the ground of the available theories according to whether the electronic relaxation times or the rotational times are the correlation times for the interaction. The comparison among systems experiencing different correlation times and electronic structures (metal ions in water, ethyleneglycol, and in proteins) allowed us to test the general theoretical approach regarding nuclear relaxation times in paramagnetic systems. Such theoretical approaches allow researchers to extract structural parameters and information on the correlation times and dynamic processes operative in the various investigated systems.

Introduction

The coupling between nuclei and unpaired electrons in a paramagnetic molecule drastically alters the nuclear NMR properties. The effects depend on parameters that are of interest from a chemical point of view: these include the metal–nucleus distance, the angles between the metal–nucleus vector and the molecular axes system, the fraction of unpaired spin density on the resonating nucleus, and other quantities related to dynamic properties of the coupled systems. For this reason extensive efforts have been made in the past to derive equations through which one could extract quantitative information on the above parameters from NMR measurements [1–11]. While the general theory for the NMR shifts induced by paramagnetic centers is now well developed [1–4], the effects on the nuclear relaxation times are far less understood in all their details. Until recently, all the available equations covered only a limited number of simple, idealized cases [5–8], and proved inadequate for the description of most real chemical systems. Now, following earlier suggestions [7, 12], the influence on the electron–nucleus coupling of changes in the electron spin energy levels due to hyperfine coupling with the metal nucleus [13] or to the zero field splitting in $S > ½$ systems [14–16], has been taken into account. Another aspect that is not understood, outside certain limit conditions, is the relationship between the nucleus–electron coupling and the coupling of the latter with the thermal bath, which is responsible for electron relaxation.

A deeper insight into the physics of these phenomena would be particularly useful for understanding solvent proton relaxation data at variable magnetic fields (Nuclear Magnetic Relaxation Dispersion, NMRD hereafter) in solutions of paramagnetic metalloproteins; indeed, this kind of measurement would in principle be able to provide detailed information on the metal chromophore, on its hydration, and on the possible role of solvent in its biological functions.

With this in mind we have measured solvent ^{1}H NMRD in the magnetic field range corresponding to proton Larmor frequencies between 0.01 and 50 MHz on ethyleneglycol solutions of $M(ClO_4)_2 \cdot 6H_2O$ (M = Co, Ni, Cu), $MnCl_2 \cdot 4H_2O$, and $GdCl_3 \cdot 6H_2O$, in the temperature range −10–+40 °C. Due to the high viscosity of ethyleneglycol the complexes rotate slower than in water, and approach the slow rotation limit at low temperature. The results are interpreted on the basis of recently developed theories, and compared with those of aqueous solutions of the above compounds, as well as with available data on metalloprotein solutions.

The investigation provided a thorough understanding of the nature of the electron–nuclear coupling in these systems.

General Considerations

It has been shown that the interaction of coordinated water protons with 3d metal ions is predominantly dipolar in origin, and that the unpaired spin density can be considered to a very good approximation to be localized onto the metal ion itself [17]. This metal-centered dipolar approximation is likely to hold also for the ethyleneglycol protons.

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TABLE I. Time Scale Ranges of Dynamic Processes Involved in the Electron–Nuclear Coupling and Energy Separations of the Spin Levels.

Process	Time constant	Time scale range (s)	Remarks
Paramagnetic contribution to nuclear longitudinal relaxation	T_{1M}	10^{-2}–10^{-7}	For protons
Chemical exchange	τ_M	∞–10^{-9}	May be comparable to either T_{1M} or τ_s, τ_r
Modulation of nucleus–electron coupling	τ_c	a	${\tau_c}^{-1} = {\tau_s}^{-1} + {\tau_M}^{-1} + {\tau_r}^{-1}$
Molecular tumbling	τ_r	10^{-6}–10^{-10}	Depends on molecular size, temperature, and solvent viscosity
Electron relaxation	τ_s	10^{-7}–10^{-13}	A time constant τ_s can be defined only when $\tau_v < \tau_s$; τ_s can be field dependent
Modulation of electron–thermal bath coupling	τ_v	10^{-10}–10^{-13}	The modulation can be caused by rotation, collisions, molecular vibrations, lattice vibrations *etc.*
Energy separations among electron and nuclear spin levels			
Nuclear Zeeman energy		1.5×10^{-5}–3×10^{-9}	From 0.01 to 50 MHz
Electron Zeeman energy		2.5×10^{-8}–5×10^{-12}	From 0.01 to 50 MHz
g-tensor anisotropy		10^{-7}–2×10^{-11}	From 0.01 to 50 MHz
Hyperfine coupling with the metal nucleus		∞–10^{-10}	
Anisotropy of hyperfine coupling		∞–10^{-10}	
Zero field splitting		∞–10^{-14}	

[a] Time scale depends on the dominant contribution to τ_c.

Therefore only the dipolar part of the electron–nuclear interaction will be considered here.

In order to better appreciate the validity conditions of the various theoretical approaches used here it may be useful to recall all the time-dependent phenomena involved in the electron–nuclear coupling process, and the different relationships among them as they depend on their relative time-scales. These processes, their time constants, and common time-scale ranges are summarized in Table I. The energy separations among the electronic levels usually encountered in paramagnetic metal ions are also reported in Table I, together with their time scales. It should be immediately stressed that the effects of such energy separations on nuclear relaxation are also dramatically dependent on their time scale relative to that of the time-dependent phenomena outlined above, as will be made clear at the end of this section.

From inspecting the time ranges of the different phenomena summarized in Table I it appears that a large variety of situations occur. Only those relevant for the cases of interest in the present research will be taken into consideration. From the very beginning it will be assumed that: 1) nuclear relaxation is much slower than the correlation time τ_c. This situation occurs in the present systems as well as in most systems of practical interest; 2) chemical exchange (in this context referred to the exchange of a coordinated solvent molecule with the bulk solution) is slower than both molecular tumbling and electron relaxation, *i.e.* $\tau_M \gg \tau_r$, τ_s. This is also a reasonable assumption in our case. On the other hand, chemical exchange may influence the observed paramagnetic contribution to the solvent nuclear relaxation rate, ${T_{1p}}^{-1}$, according to the following relationship

$$ {T_{1p}}^{-1} = f(T_{1M} + \tau_M)^{-1} \qquad (1) $$

where f is the molar fraction of the solvent protons interacting with the paramagnetic center. The correlation time τ_c will be considered to be dominated by either τ_r or τ_s. Furthermore, the relationship between these two parameters and the time scale of the energy separations of the electronic spin levels will be considered in detail.

As far as electron relaxation is concerned, it is useful to divide the investigated metal complexes into 'slow relaxing' (Cu^{2+}, Mn^{2+}, Gd^{3+}) and 'fast relaxing' (Co^{2+}, Ni^{2+}) systems, the electronic relaxation times of the former being in the range 10^{-8}–10^{-10} s and those of the latter in the range 10^{-11}–10^{-12} s.

A still unresolved problem in the analysis of the fast relaxing metal ions is whether it is possible to treat these systems as having a single electronic relaxation time constant, or whether they should be regarded as having a distribution of electronic relaxation times [18]. Even the very definition of relaxation time can be questioned. In this work a pragmatic approach to the problem will be attempted in the light of the NMRD data on such systems and of the predictions of recently developed theories [14–16, 19].

Experimental

$M(ClO_4)_2 \cdot 6H_2O$ salts were prepared from analytical grade metal carbonates and recrystallized from water. $MnCl_2 \cdot 4H_2O$ and $GdCl_3 \cdot 6H_2O$ were analytical grade and used as such. Analytical grade ethyleneglycol (water content $<0.1\%$) was also used as such from a freshly opened bottle. Ethyleneglycol solutions were made by dissolving the compounds previously dried under vacuum. Under these conditions the above metal ions are probably largely coordinated by the ethyleneglycol solvent, although some water molecules are likely to be retained in the first coordination sphere. For interpretation of the experimental data the precise knowledge of the donor set of each compound is not required, as long as the interaction of the solvent protons with the paramagnetic center is strong enough to be detected. This apparently is the case for all the complexes investigated. At the low salt concentrations used coordination of chloride ions to Mn^{2+} and Gd^{3+} can also be considered negligible [20].

Throughout this paper the T_{1p}^{-1} data will be reported as relaxivity, *i.e.* normalized to 1 mM metal concentration, irrespective of the solvent. The G values, which depend on the molar fraction of protons interacting with the paramagnetic center (see later), are corrected for the slight difference between the molarity of the bulk protons in ethyleneglycol (107 M) and water (111 M).

^1H NMRD spectra in the 0.01–50 MHz proton Larmor frequency range were run in the −10–+40 °C temperature range on the field-cycling instrument at the IBM T. J. Watson Research Center of Yorktown Heights, N.Y.

The paramagnetic contributions to the solvent proton relaxation rates were estimated in each case by subtracting the relaxation rate of solutions of the diamagnetic zinc(II) analogue at the same concentration and temperature. The latter were however always indistinguishable from the relaxation rates of the pure solvent.

The field-cycling technique does not allow resolution of the individual relaxation times of the methylene and hydroxide protons of ethyleneglycol. Therefore the proton relaxation time at each field was measured as the time constant for the return to equilibrium of the overall proton magnetization of the sample, assuming a single exponential decay. Previous T_1 measurements on a standard high resolution instrument [21] have shown that the relaxation rates of methylene and hydroxide protons in ethyleneglycol solutions of paramagnetic complexes differ by about 20%. The difference might be larger if the ions were mainly surrounded by water molecules, since in this case the paramagnetic effect would only be propagated to the hydroxide protons of ethyleneglycol. In any case, it has been shown [22] that even exponential decays differing by a factor of two can be treated as a single exponential decay with a time constant equal within 1% to the average of the two time constants.

Results and Discussion

The results can be better presented if divided into two sets according to whether the metal ion displays slow (copper(II), manganese(II), and gadolinium(III)) or fast electronic relaxation times (nickel(II), cobalt(II)). In the latter case the correlation time for the dipolar coupling between unpaired electrons and nuclei is the electronic relaxation time under any circumstance (this holds rigorously as long as the electron–lattice coupling is not modulated by molecular tumbling, see above). In the former the correlation time can be either the electronic relaxation time or the rotational time depending on the viscosity of the solution. The two cases provide different information and are instructive in order to understand the different limits of the theoretical approach.

Slow Relaxing Ions

Gadolinium(III)

Gadolinium(III) is an f^7 ion with half-filled configuration and $S = 7/2$. There is no other excited state with such spin multiplicity and this accounts for the slow electronic relaxation times of gadolinium(III) with respect to the other paramagnetic lanthanide ions. Indeed, the EPR signal of Gd^{3+} is relatively narrow and in NMR it is an excellent relaxing probe.

The solvent ^1H NMRD of an ethyleneglycol solution containing $GdCl_3$ is reported in Fig. 1 at three different temperatures. For comparison purposes the data of a Gd^{3+} solution in water is also reported [23]. The interpretation of these curves is attempted in the assumption that $\tau_M \ll T_{1M}$, *i.e.* the solvent exchange is rapid on the NMR time scale. This has been shown to be the case for coordinated water [24], and can be initially assumed to be also true for ethyleneglycol.

TABLE II. Best Fit NMRD Parameters[a] for Gd^{3+} and Mn^{2+} Solutions.

T (°C)	G (cm^{-6})[b]	τ_{s0} (s)[c]	τ_{s50} (s)[d]	τ_v (s)[e]	τ_r (s)[f]
Gd^{3+} in ethyleneglycol					
39	1.2×10^{46}	7.7×10^{-11}	9.0×10^{-9}	3.3×10^{-11}	2.6×10^{-10}
25	1.3×10^{46}	9.9×10^{-11}	2.6×10^{-8}	4.9×10^{-11}	3.7×10^{-10}
−9	3.7×10^{45}	4.0×10^{-10}	1.7×10^{-7}	6.3×10^{-11}	2.0×10^{-9}
Gd^{3+} in water					
25	1.8×10^{46}	1.2×10^{-10}	3.6×10^{-9}	1.6×10^{-11}	4.5×10^{-11}
Mn^{2+} in ethyleneglycol					
39	1.5×10^{46}	1.4×10^{-10}	5.2×10^{-8}	5.9×10^{-11}	3.1×10^{-10}
25	1.8×10^{46}	1.4×10^{-10}	6.8×10^{-8}	6.7×10^{-11}	4.1×10^{-10}
−9	8.0×10^{45}	5.0×10^{-10}	1.4×10^{-7}	5.1×10^{-11}	3.4×10^{-9}
Mn^{2+} in water					
25	3.0×10^{46}	3.5×10^{-9}	1.5×10^{-8}	5.3×10^{-12}	3.2×10^{-11}

[a] Standard deviations within 10%. [b] Defined in the text. [c] Electronic relaxation time at zero field. [d] Electronic relaxation time at magnetic field corresponding to 50 MHz proton Larmor frequency (eqn. 2). [e] Correlation time for the electron–thermal bath interaction (eqn. 2). [f] Rotational correlation time of the solvated ion.

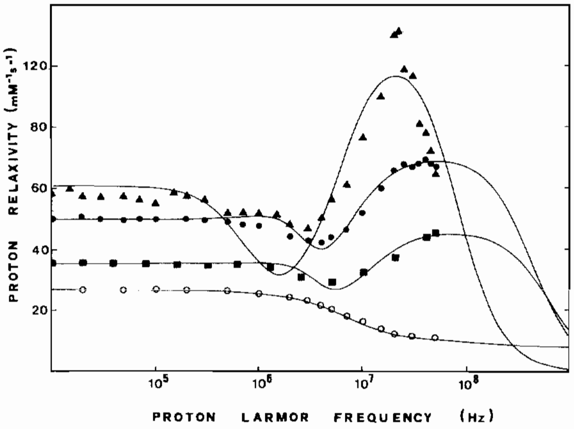

Fig. 1. Solvent proton relaxivities as a function of field for ethyleneglycol solutions of $GdCl_3 \cdot 6H_2O$ at −9 (▲), 25 (●), and 39 °C (■) as compared to those of water solutions at 25 °C (○) [23]. The best fit curves are calculated with the parameters of Table II.

The experimental data, which are directly related to T_{1M}^{-1}, do not follow the expected patterns when a proton nucleus is coupled with an unperturbed S manifold, the correlation time for the coupling being field independent (Solomon's approach [5]). Such treatment predicts the decrease in relaxivity observed around 1 MHz to be 7/10 of the initial values, whereas in water such a decrease is definitely smaller and in ethyleneglycol the dispersion is hardly apparent and the relaxivity tends to increase at high field. The first correction with respect to Solomon's approach is to consider that τ_c is not field-independent. As in manganese(II) (*vide infra*), it is proposed that τ_s is field dependent; if the dependence is due to modulation of the quadratic zero-field-splitting, then τ_s can be described by the following expression [25–27].

$$\tau_s^{-1} = 1/(5\tau_{s0})((1/(1 + \omega_s^2\tau_v^2) + (4/(1 + 4\omega_s^2\tau_v^2)) \qquad (2)$$

The best fitting parameters for the NMRD profiles are reported in Table II. It appears that the major difference between the water and ethyleneglycol data is due to the difference in rotational time. In water solutions [23] at low field τ_r is close to τ_s, although slightly smaller; τ_c is thus determined by a combination of the two. When τ_s starts to increase (above 1 MHz) it causes a slight increase in τ_c and therefore a decrease in relaxivity that is slightly smaller than the 7/10 expected on the basis of Solomon's theory [5]. In ethyleneglycol, τ_r is expected to be much larger than in water and larger than τ_s at low field; therefore the increase in τ_s with field causes an increase in relaxivity until τ_s reaches the τ_r values. It may also happen that the ω_I dispersion starts before the τ_r value is reached and this causes a sharp peak in the dispersion as in the profile at −9 °C in Fig. 1. However, the fitting at −9 °C is not satisfactory.

If we discard for the moment the data at −9 °C, a comparison of the best fit parameters with those obtained in water solution can be attempted. First, it can be noted that the calculated τ_r values are

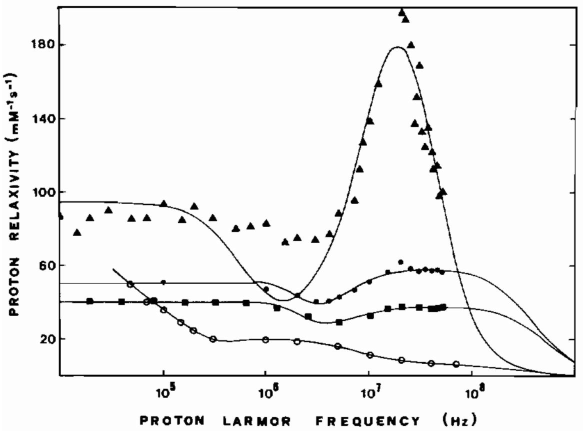

Fig. 2. Solvent proton relaxivities as a function of field for ethyleneglycol solutions of $MnCl_2 \cdot 4H_2O$ at −9 (▲), 25 (●), and 39 °C (■) as compared to those of water solutions at 25 °C (○) [28]. The best fit curves are calculated with the parameters of Table II.

indeed about one order of magnitude longer in ethyleneglycol than in water at the same temperature. The latter is about 1.5 times longer than the rotational correlation times of hexaaqua-3d metal ions, probably on account of the larger size of the Gd^{3+} complex due to both a longer metal–oxygen distance and to a larger hydration number. The G value of 1.8×10^{46} cm^{-1} may be consistent with 8–9 coordinated water molecules and metal proton distances of 3.1–3.2 Å [23]. Now,

$$G = \sum_i n_i/r_i^6 \qquad (3)$$

where n_i is the number of protons interacting with the metal ion at distance r_i. The donor set of Gd^{3+} in ethyleneglycol is not known; G values of the same order of magnitude as that obtained in water indicate that the overall paramagnetic effect is propagated to the solvent, either by direct coordination or by exchange of the hydroxide protons, and the exchange is fast on the NMR time scale.

Interestingly, the τ_v parameter is longer in ethyleneglycol than in water. In the frame of eqn. 2, τ_v is related to collisions of solvent molecules with the solvated ion; such motions are also apparently slowed down in viscous solvents. On the other hand τ_{s0}, *i.e.* the electronic relaxation time at zero field, which is only related to the magnitude of the instantaneous zero field splitting induced by collisions, does not change much from water to ethyleneglycol.

In the light of the above discussion the NMRD data at −9 °C can be examined in more detail. Although the fitting is poor, both τ_v and τ_r show the expected increase due to the decrease of thermal motion and to the increase in viscosity of the solution. However a much smaller G value is obtained. A possible cause of deviation could be a contribution of τ_M to T_{1M}, *i.e.* a slowing down of the solvent exchange rate. If neglected, this would simulate a smaller G value and would qualitatively account for the bad fit around 2 and 20 MHz. However, this possibility can be ruled out by including τ_M as a parameter in the best fitting procedure. Another source of error may be the neglect of a possible small static zero field splitting. For example, a zero field splitting of 0.03 cm^{-1} would not influence much the data at 25 and 39 °C but would give a sizeable contribution at −9 °C owing to the longer τ_c. The latter contribution is however expected to simulate larger G values [9, 13, 27]. Larger G values would also be simulated by neglect of hyperfine coupling with the metal nucleus. In any case, this effect is expected to be relatively small for gadolinium, which has only 30% of NMR-active isotopes. It seems therefore that a smaller G value at −9 °C may reflect a real change in the geometry of the complex. Indeed, smaller G values at −9 °C are also observed in Mn^{2+} and Cu^{2+} solutions.

Manganese(II)

The NMRD of ethyleneglycol solutions of $Mn(H_2O)_4Cl_2$ are shown in Fig. 2, together with the profile in H_2O. The latter shows a dispersion at ~0.1 MHz which is assigned to a contact contribution to the coupling [28]. The usual ω_s dispersion for the dipolar coupling occurs at ~8 MHz. The contact contribution is not apparent in ethyleneglycol solutions, probably because the dipolar contribution increases, owing to the increase of τ_r. The curves are fitted with a procedure analogous to that used for $GdCl_3$. The results are shown in Table II. The data are qualitatively very similar to those of Gd^{3+}: again, the fitting at 25 and 39 °C is reasonably good, while that at −9 °C is less satisfactory. The best fit parameters are also relatively similar, with G at −9 °C being sizeably smaller, and most of the considerations made for Gd^{3+} also hold here.

Apparently τ_{s0} is longer for Mn^{2+} than for Gd^{3+}; this would imply slightly smaller distortions of the coordination sphere of the ion upon collision with solvent molecules. It should be mentioned that besides possible contributions from static zero field splitting, hyperfine coupling with the metal nucleus may also drastically affect the Mn^{2+} NMRD data. The latter can be estimated to be of the order of 10^{-2} cm^{-1}, and therefore to influence mainly the data at −9 °C. However neglect of this contribution, just like zero field splitting, would be expected to simulate larger G values. Therefore, a smaller G value at −9 °C seems again to be a characteristic of the solvated ion rather than an artifact due to inadequacy of the theory.

TABLE III. Best Fit NMRD Parameters for Cu^{2+} Complexes in Ethyleneglycol.[a]

T (°C)	G (cm^{-6})	τ_c (s)
39	9.4×10^{45}	3.7×10^{-10}
25	1.1×10^{46}	4.5×10^{-10}
15	1.3×10^{46}	5.7×10^{-10}
5	9.9×10^{45} (6.3×10^{45})	1.1×10^{-9} (1.8×10^{-9})
−9	5.9×10^{45} (5.7×10^{45})	2.7×10^{-9} (2.8×10^{-9})

[a] See notes to Table II. The parameters are calculated with $g = 2.15$ and an isotropic A value of 26×10^{-4} cm^{-1}. The values in parenthesis are calculated by fitting the high field data to the Solomon equation.

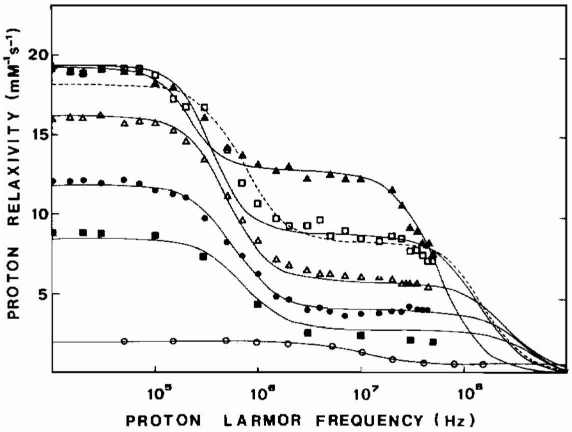

Fig.3. Solvent proton relaxivities as a function of field for ethyleneglycol solutions of $Cu(ClO_4)\cdot 6H_2O$ at −9 (▲), 5 (□), 15 (△), 25 (●), and 39 °C (■) as compared to those of water solutions at 25 °C (○) [28]. The solid lines are best fit curves obtained using an isotropic A value (or the Solomon equation for the water solution [28]); the dashed line is the best fit curve of the data at 5 °C using anisotropic A values. The best fit parameters are reported in Table III.

Copper(II)

The NMRD of water solutions containing copper(II) at 25 °C (Fig. 3) are interpreted on the basis of simple Solomon's approach [28]. We have shown, however, that in copper complexes hyperfine coupling with the metal nucleus can affect the NMRD profile at low magnetic fields when $|A|$ isotropic or $|A_{\parallel}|$ is larger than $\hbar\tau_c^{-1}$ [13, 15]. Here τ_c is 3×10^{-11} s and the above condition does not hold. The NMRD profile of copper(II) solutions in ethylene glycol at 39 °C is similar to that in water, although τ_c is now 4×10^{-10} s which compares with 3×10^{-11} s in water at 25 °C. In both cases τ_c is determined by τ_r. The profiles at 25, 15, 5, and −9 °C increasingly deviate from Solomon in that the decrease in relaxivity due to the ω_S dispersion around 0.5 MHz is less than 7/10. This is due to the hyperfine splitting of the S manifold. We know, however, that above ~4 MHz Solomon's equation holds, since the value of $|A|$ is such that it is smaller than $g\beta H$ and does not affect the T_1^{-1} profile. The fitting of the data points above 4 MHz at the temperatures where an ω_I dispersion can be observed (−9 and 5 °C) provides τ_c values consistent with the temperature pattern and with the values obtained for the other systems (Table III), but somewhat smaller G values.

At magnetic fields lower than 4 MHz the increase in T_1^{-1} is smaller than expected on the basis of Solomon's approach. The system probably experiences anisotropic A values due to partial solvation of the hexaaqua system, and therefore a fitting of the whole NMRD profile should be attempted on the ground of the appropriate equation [13]. However, the observed relaxivity should be an average among those of each contributing proton having metal–nucleus vector forming different angles with the z axis of the A tensor. Owing to the uncertainty in the determination of such angles and to the lack of generality of the system, we have first fictitiously described the system with an isotropic A value. Such fittings are shown in Fig. 3. The pattern of the best fitting τ_c values (Table III) is similar to that estimated from the analysis of the high field region, while the G values are higher (again with the exception of that at −9 °C) and closer to those of the other systems. The best fitted A value is 26×10^{-4} cm^{-1}, which is a typical value for a CuO_6 chromophore [29]. As an example, a fitting of the data at 5 °C with anisotropic A values ($A_{\parallel} = 120 \times 10^{-4}$, $A_{\perp} = -20 \times 10^{-4}$ cm^{-1}) and a spherical distribution of protons around the metal ion is also reported in Fig. 3 (dashed line). Interestingly, the inflection around 0.5 MHz is now calculated at too high field, while that obtained with isotropic A was at too low field with respect to the experimental points. This might indicate the presence of a contribution from anisotropic species to an essentially isotropic system.

The whole NMRD curves could be qualitatively fitted by using the simple Solomon's approach and increasing τ_M with decreasing temperature according to equation 1. However, the fitting is bad in any case and the required values of τ_M would be too long,

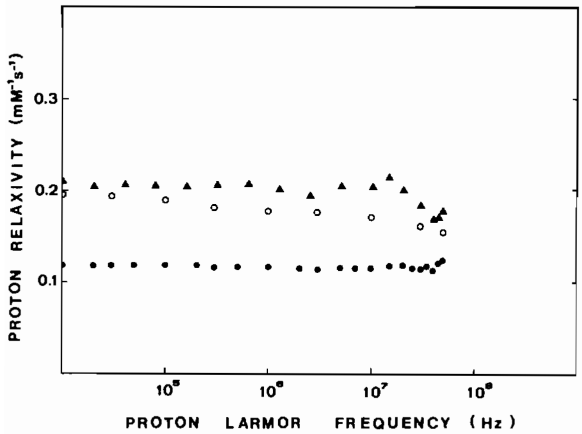

Fig. 4. Solvent proton relaxivities as a function of field for ethyleneglycol solutions of $Co(ClO_4)\cdot 6H_2O$ at –9 (▲) and 25 °C (●) as compared to those of water solutions at 25 °C (○) [15].

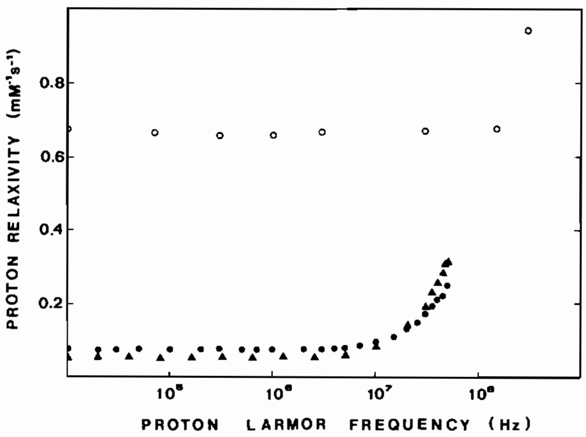

Fig. 5. Solvent proton relaxivities as a function of field for ethyleneglycol solutions of $Ni(ClO_4)\cdot 6H_2O$ at –9 (▲) and 25 °C (●) as compared to those of water solutions at 25 °C (○) [11].

e.g. of the order of 10^{-2} s at 25 °C. In the manganese system τ_M can be set to be shorter than 10^{-6} s at 25 °C.

Fast Relaxing Systems

Cobalt(II)

Hexaaquacobalt(II) perchlorate in ethyleneglycol at both 25 °C and –9 °C shows an essentially flat NMRD profile (Fig. 4). The same happens in water at 25 °C (in the same Figure). These patterns can be accounted by considering that τ_c is determined by τ_s in every case and that the ω_s dispersion occurs above 40 MHz. The upper limit for τ_s can be set around 10^{-11} s. The relatively low relaxivity values are due to the short τ_s. Although in the absence of a dispersion in the NMRD profile no fitting can be performed and therefore τ_c and G values for the complexes cannot be obtained, the normalized T_1^{-1} values of water and ethyleneglycol solutions are similar. Therefore, assuming similar G values the τ_s values are also expected to be similar. If G values of the order of those of copper or manganese complexes are assumed, τ_s at 25 °C can be estimated to be about 3×10^{-12} s from the Solomon equation, or up to 6×10^{-12} s from the equation including the effects of possible static zero field splittings [14]. At –9 °C the relaxivity is about twice that at 25 °C and therefore the above argument would place τ_c around 10^{-11} s. If so, the slight decrease of the relaxivity between 20 and 40 MHz would be accounted for by the beginning of the ω_s dispersion.

Nickel(II)

Hexaaquanickel(II) perchlorate in ethyleneglycol gives rise to an NMRD profile characterized by a constant value up to 4–10 MHz and then by an increase (Fig. 5), whose maximum could not be located. It has been shown that nickel(II) complexes do not give rise to any ω_s dispersion because of the presence of zero field splitting [7, 11, 15, 16]. This accounts for the flat part of the profile. The increase above 10 MHz, which has also been observed in water (Fig. 5) between 50 and 300 MHz, is due to the field dependence of τ_s as observed for manganese(II) and gadolinium(III). Since no maximum is observed, no quantitative fitting could be attempted. At variance with the cobalt(II) case, there is a large difference in relaxivity at low field between water and ethyleneglycol solutions. If the G values are similar, this implies τ_{s0} values one order of magnitude shorter for the Ni^{2+} ion in ethyleneglycol. Since τ_{s0} is inversely proportional to the square of the zero field splitting of the electronic levels, it appears that the chromophore is somewhat more distorted in the latter case.

Conclusions

It is important to note that all the variety of solvent ^1H NMRD profiles is fully accounted and understood on the basis of the electronic properties of the metal ion. The NMRD profiles of slow relaxing metal ions are quite dependent on the environment of the metal ion. In ethyleneglycol at 39 °C they are reminiscent of those in water, because the rotational times are similar in the two cases. The profiles relative to ethyleneglycol solutions at lower temperatures are similar to those of metalloproteins because again the rotational times are similar. In particular the NMRD profile of gadolinium(III) in ethyleneglycol at 25 °C (Fig. 1) is similar to that of gadolinium(III) concanavalin A in water at 25 °C (Fig. 6) [30] and the profile of manganese(II) in ethyleneglycol at –9 °C (Fig. 2) is similar

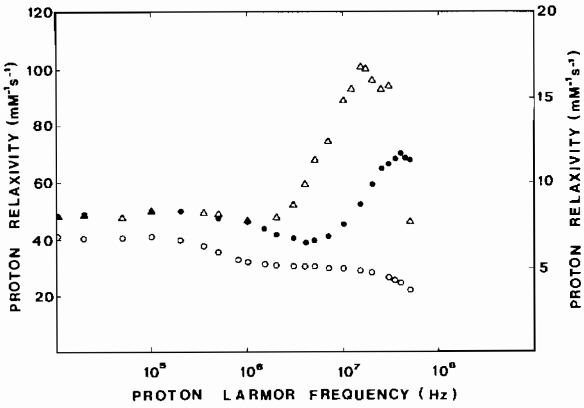

Fig. 6. Water proton relaxivities as a function of field for solutions of manganese(II) Concanavalin A (△, left hand scale) [31], Gadolinium(III) concanavalin A (●, left hand scale) [30], and Copper(II) carbonic anhydrase (○, right hand scale) [32] at 25 °C.

to that of manganese(II) concanavalin A at 25 °C (Fig. 6) [31]. In the latter case any attempt of interpretation on the basis of Solomon's equation and field dependence of τ_s overestimated the hydration of the metal ion [27]. It has been shown that the inclusion of the zero field splitting of the $S = 5/2$ manifold in a qualitative way does not reduce G to reasonable values [27]. We ascribe such behavior to the non-inclusion of the effects of hyperfine coupling with the manganese nucleus. Finally, the NMRD profile of copper(II) in ethyleneglycol at −9 °C (Fig. 3) is similar to that of copper(II) carbonic anhydrase at 25 °C (Fig. 6) [32].

As far as the fast relaxing metal ions are concerned, the observation that the electronic relaxation times of Co^{2+} are very short and similar in water and ethylene glycol solutions has important implications on the nature of the electron relaxation mechanisms. For ions with $S > 1/2$ it is customarily assumed that such mechanisms arise from modulation of the zero field splitting, either through rotation if a static zero field splitting is present or through induction of transient zero field splitting by collision with solvent molecules. In both cases such mechanisms would depend heavily on the viscosity of the solvent, which is not experimentally observed. Moreover, the correlation time for electron relaxation would be either τ_r or τ_v which, even in water, are longer than 10^{-11} s. Therefore, electronic relaxation times shorter than 10^{-11} s would imply that the systems were in the so-called non-Redfield limit. We have recently shown that in such cases the systems would behave as if experiencing an 'effective' electronic relaxation time very close to the correlation time itself [19], *i.e.* longer than 10^{-11} s. Apparently, other mechanisms independent of these kind of motions in solution have to be operative. Such mechanisms could be of solid state type, like Orbach processes; the only requirement would then be the availability of low-lying excited states coupled to the ground state through lattice vibrations.

On the other hand, the observation of a large increase in relaxivity at high field in Ni^{2+} solutions supports the idea that zero field splitting modulation is the dominant electron relaxation mechanism for such ions. A possible explanation for the large differences in relaxivity between water and ethylene glycol solutions could be that in water only transient zero field splitting is present induced by collisions with solvent molecules with correlation time τ_v, while in ethylene glycol there is a dominant contribution from the modulation of the static zero field splitting by rotation.

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References

1 H. M. Mc Connell and D. B. Chesnut, *J. Chem. Phys., 28,* 107 (1958).
2 R. J. Kurland and B. R. McGarvey, *J. Magn. Reson., 2,* 286 (1970).
3 B. Bleaney, *J. Magn. Reson., 8,* 91 (1972).
4 R. M. Golding, R. O. Pascual and J. Vrbancich, *Mol. Phys., 31,* (1976).
5 I. Solomon, *Phys. Rev., 99,* 449 (1955).
6 N. Bloembergen, *J. Chem. Phys., 27,* 575 (1957).
7 U. Lindner, *Ann. Physik, 16,* 319 (1965).
8 H. Pfeiffer, D. Michel, D. Sames and H. Sprinz, *Mol. Phys., 11,* 591 (1966).
9 S. H. Koenig, *J. Magn. Reson., 31,* 1 (1978).
10 S. H. Koenig, *J. Magn. Reson., 47,* 441 (1982).
11 H. L. Friedman, H. G. Hertz, M. Holtz and F. Hirata, *J. Chem. Phys., 73,* 6031 (1980).
12 M. E. Fabry (Riepe), S. H. Koenig and W. E. Shillinger, *J. Biol. Chem., 245,* 4256 (1970).
13 I. Bertini, F. Briganti, C. Luchinat, M. Mancini and G. Spina, *J. Magn. Reson.,* in press.
14 I. Bertini, C. Luchinat, M. Mancini and G. Spina, *J. Magn. Reson., 59,* 213 (1984).
15 I. Bertini, C. Luchinat, M. Mancini and G. Spina, in D. Gatteschi, O. Kahn and R. D. Willet, (eds.), 'Magneto-Structural Correlations in Exchange Coupled Systems', Reidel, Dordrecht, 421 (1985).

16 (a) N. Benetis, J. Kowalewski, L. Nordenskiöld, H. Wennerström and P.-O. Westlund, *Mol. Phys., 48,* 329 (1983);
(b) N. Benetis, J. Kowalewski, L. Nordenskiöld, H. Wennerström and P.-O. Westlund, *J. Magn. Reson., 58,* 261 (1984);
(c) P.-O. Westlund, H. Wennerström, L. Nordenskiöld, J. Kowalewski and N. Benetis, *J. Magn. Reson., 59,* 91 (1984).

17 L. Nordeskiöld, A. Laaksonen and J. Kowalewski, *J. Am. Chem. Soc., 104,* 379 (1982).

18 D. T. Pegg and D. M. Doddrell, *Aust. J. Chem., 29,* 1869; 1885 (1976).

19 I. Bertini, C. Luchinat and J. Kowalewski, *J. Magn. Reson.,* in press.

20 L. G. Sillèn and A. E. Martell, 'Stability Constants of Metal-ion Complexes', Supplement No. 1, Chem. Soc. Special Publ., No. 25, The Chemical Society, London, 1971.

21 I. Bertini, G. Lanini, C. Luchinat, M. Mancini and G. Spina, *J. Magn. Reson.,* in press.

22 S. H. Koenig and R. D. Brown, personal communication.

23 S. H. Koenig and M. Epstein, *J. Chem. Phys., 63,* 2279 (1975).

24 J. Reuben, *J. Chem. Phys., 63,* 5063 (1975).

25 N. Bloembergen and L. O. Morgan, *J. Chem. Phys., 34,* 842 (1961).

26 M. Rubinstein, A. Baram and Z. Luz, *Mol. Phys., 20,* 67 (1971).

27 S. H. Koenig and R. D. Brown, in I. Bertini and R. S. Drago (eds.), 'ESR and NMR of Paramagnetic Species in Biological and Related Systems', Chap. 4, Reidel, Dordrecht, 1980.

28 R. Hausser and F. Noack, *Z. Phys., 182,* 93 (1964).

29 A. Bencini and D. Gatteschi, *Transition Met. Chem., 8,* 1 (1982).

30 S. H. Koenig, C. Baglin, C. F. Brewer and R. D. Brown, *J. Magn. Reson. Med. Biol.,* in press.

31 S. H. Koenig, R. D. Brown and C. F. Brewer, *Proc. Nat. Acad. Sci. U.S.A., 70,* 475 (1973).

32 I. Bertini and C. Luchinat, in K. D. Karlin and J. Zubieta (eds.), 'Biochemical and Inorganic Aspects of Copper Coordination Chemistry', Adenine, in press.