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DIVALENT PARAMAGNETIC COUNTERIONS SITE BINDING IN POLYELECTROLYTE SOLUTIONS.
ANALYSIS OF THE FREQUENCY DEPENDENCE OF THE WATER PROTONS MAGNETIC RELAXATION AND THE CHARACTERISTIC PARAMETERS OF "SITE BINDING"

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Chemical shift and relaxation time measurements on the water protons in polyelectrolyte solutions containing divalent paramagnetic counterions have shown the existence of three types of counterions: – site bound with loss of water molecules and partial or complete release of the electrostriction in the first hydration sphere, – atmospherically trapped with no change in hydration, – free. The overall stoichiometry of the two former is in agreement with Manning's fraction of condensed counterions. A complete analysis of the frequency dependent contribution of site bound counterions to the water protons relaxation times leads us to interesting conclusions on the modifications of the first hydration shell and on the life time of site binding.

1. Introduction

A clear understanding of the counterion-polyion interaction in polyelectrolyte solutions and particularly of the problem of ionic selectivity of highly charged polyelectrolytes requires us to go beyond the thermodynamic treatment [1–3] and to describe in more detail the physical state of the considered counterions. Volumetric [4], acoustic [5] and potentiometric [6] measurements have been used for this purpose. We have recently shown that an extension of magnetic resonance techniques which were developed for the study of ion binding to discrete sites of biological macromolecules [7] can be of great use in studies of homopolyelectrolytes. The state of the divalent paramagnetic ions added to the tetramethylammonium (TMA) salt of a polyelectrolyte can be characterized through the chemical shift and relaxation times of the water protons. Due to rapid exchange, the change in bulk water proton resonance reflects the perturbation in the hydration sphere of the paramagnetic ion. Chemical shift will essentially reflect the change in number and distance of water molecules in the first hydration shell. Relaxation times will depend both on the hydration and motions of the paramagnetic counterion.

By adding Co^{2+} cations to the polyelectrolyte salt, we have already shown [8,9] that the chemical shift of the water protons reveals the existence of at least two successive types of counterions. The first type corresponds to about half the total condensed fraction predicted according to Manning's electrostatic theory [3]. The second type has characteristics close to that of a free counterion. Under the same conditions, i.e. the addition of Mn^{2+} cations to the polyelectrolyte salt, relaxation measurements distinguish qualitatively between three successive types of ions. The first fraction corresponds to that found in chemical shift measurements. The sum of the first and second corresponds to the total condensed fraction. The third type has the same influence on water relaxation as free ions [10]. We have therefore proposed the identification of these three types as "site bound", "atmospherically trapped" and "free" counterions.

A systematic study of the frequency dependence of the relaxation times is required in order to extract quantitatively some hydration and mobility parameters from the relaxation data and to compare them with the results of the chemical shift experiments. We have chosen for such a study a series of four polyelectrolytes with a very similar value of the linear charge density parameter $\lambda = e^2/\epsilon kTb$ (where b is the mean distance between charges along the polymer axis and ϵ the dielectric constant of water) close to 3. Polyphosphate and Gantrez (an alternating copolymer of maleic anhydride and vinylether) have been used in our previous studies of chemical shift and relaxation at a single frequency [10]. They are known to strongly affect the hydration of site bound counterions. From previous chemical shift measurements [8] polyacrylic acid is known to produce site binding with a smaller effect on hydration. Polystyrene sulfonic acid on which no shift or relaxation studies had yet been performed, was believed, from volumetric studies [4], to produce essentially no site binding. Complementary EPR measurements on the Mn^{2+} ion have been performed on the four polymers.

2. Experimental procedures

2.1. Polyelectrolytes

Polyphosphate (PP) (gift of U.P. Strauss), Polyacrylate (PA) (K and K), Polystyrene sulfonate (PSS) (Dow Chemical Co) and Gantrez (Borden Chem. Co) were high molecular weight samples. They have been put in acid form, the three former by passage through ion exchange resins, and the latter by mild hydrolysis at 60°C. After titration of aliquots by TMA OH, exact neutralisation of the solutions has been carried out.

A series of solutions was prepared for each polysalt by adding water and the chloride of a divalent paramagnetic ion, the ratio of water to chloride being chosen to keep constant the final polyelectrolyte concentration and to obtain the desired value of the ratio $R = 2[M^{2+}]/[TMA^+]$ which has been varied in a series from 0 to 1.6. Depending on the polyelectrolyte and its concentration, precipitation may arise for $R \sim 1$.

2.2. Chemical shift measurements

Chemical shift measurements have been carried out on standard CW high resolution NMR instruments (Varian HA 100 or CAMECA 250 MHz). Co^{2+} is used for chemical shift measurements due to its high electronic relaxation rate ($\tau_s \sim 10^{-12}$ s) which minimizes its contribution to water proton line broadening. Since line broadening at higher fields overcomes the gain in absolute frequency shift, the stability and the precision in frequency determination is the main criterion for the choice of an instrument. In order not to introduce an ionic marker into the solution, chemical shifts are measured with respect to the signal of a benzene capillary. The correction for paramagnetic susceptibility is derived from a measurement of Co^{2+} solutions in the absence of polyelectrolyte and in the presence of 2,2-dimethyl-2-silapentane-5-sodium sulfonate (DSS) as a marker.

2.3. Water relaxation measurements

Longitudinal (T_1) and transverse (T_2) relaxation times have been measured on a Bruker SXP pulse spectrometer working in the 4–90 MHz range. For T_1 measurements by the inversion recovery method, the whole free induction decay (FID) was recorded for at least 25 values of the time between the 180° and 90° pulses. The relative changes in height were measured at different positions on the FID to ensure the absence of field drifts or phase changes during the experiment. For T_2 measurements, a Carr-Purcell-Meiboom-Gill sequence was used. Programs for the acquisition and the treatment of the data have been written for the Nicolet BNC 12 minicomputer. The calculated semi-log plots are superposed on the experimental points on the oscilloscope for optimization of phase adjustments in T_2 measurements and for inspection of the final agreement for T_1 and T_2. For these relaxation measurements Mn^{2+} has been used because of its longer electronic relaxation time ($\tau_s \sim 10^{-9}$ s). The concentrations in Mn^{2+} and polyelectrolyte are in the range of 10^{-3} M, roughly ten fold more dilute than in the chemical shift experiments.

2.4. EPR measurements

EPR measurements have been performed at X band using a dual cavity with a flat quartz cell for aqueous solutions.

3. Experimental results

3.1. Chemical shift

The results of chemical shift measurements for PP, Gantrez and PA have been already published [8,10]. We give in fig. 1a the result obtained for PSS and recall in fig. 1b the result obtained for PP in order to stress the extreme cases for both the differences in the slopes relative to Co^{2+} in the absence of polyelectrolyte and the amplitudes of the TMA chemical shifts. The slopes expressed in terms of an apparent number *n* of water molecules subjected to the influence of the paramagnetic counterion (6 for Co^{2+} in the absence of polyelectrolyte) are given in table 1.

3.2. Relaxation measurements

Typical plots of $1/T_1$ and $1/T_2$ versus the concentration in Mn^{2+} are given in fig. 2 for PSS and PA. Corresponding plots for PP and Gantrez have already been published [10]. The NMR frequency displayed is that at which the distinction between the two or three different states of the counterion is the most evident. The coincidence of the first break in the curves as a function of *R* with the fraction found in the chemical shift experiments favours an interpretation in term of "site binding".

We shall be essentially concerned by the quantitative analysis of the relaxation in the low *R* region ($R < 0.4$) to obtain information on the hydration and mobility of the first added counterions. This can be obtained from the frequency dependence of their contribution to the water relaxation rates, derived from the initial slope of T_1^{-1} and T_2^{-1} versus *R*, and expressed as:

Table 2
Slopes of the water chemical shift in presence of Co^{2+} salts expressed in terms of the number n of water molecules subjected to Co^{2+} scalar interaction

Cl_2Co	PSS-Co	PA-Co	PP-Co	Gantrez-Co
6	6	~1.5	~0	~0

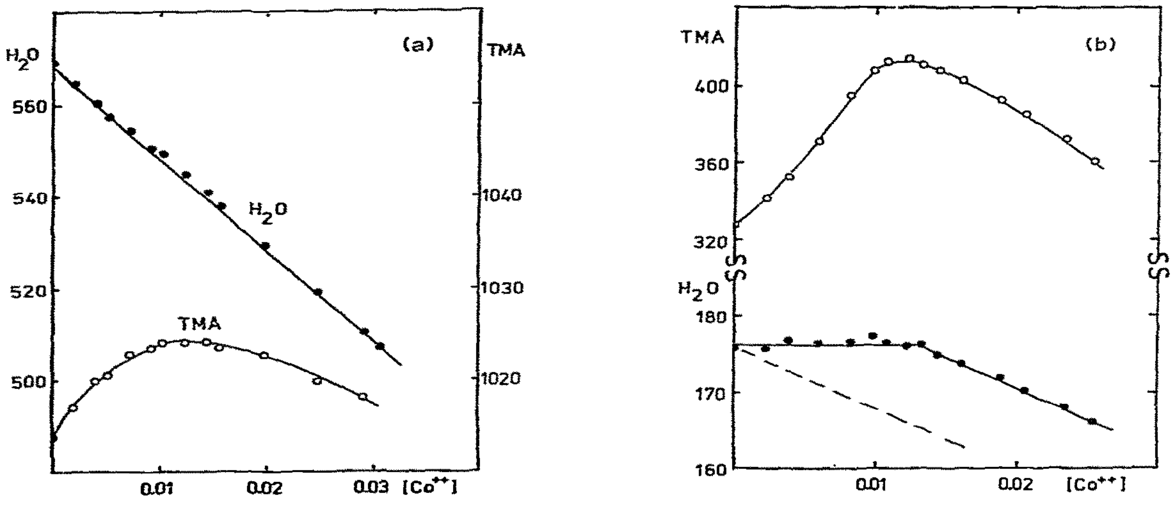


Fig. 1. Water proton (●) and TMA protons (○) chemical shift as a function of the molar concentration of Co^{2+} ions. The chemical shift in absence of polyelectrolyte is given by the straight line in a) and the dotted line in b). a): in the presence of PSS 0.049 N (250 MHz); b): in the presence of PP 0.051 N (100 MHz).

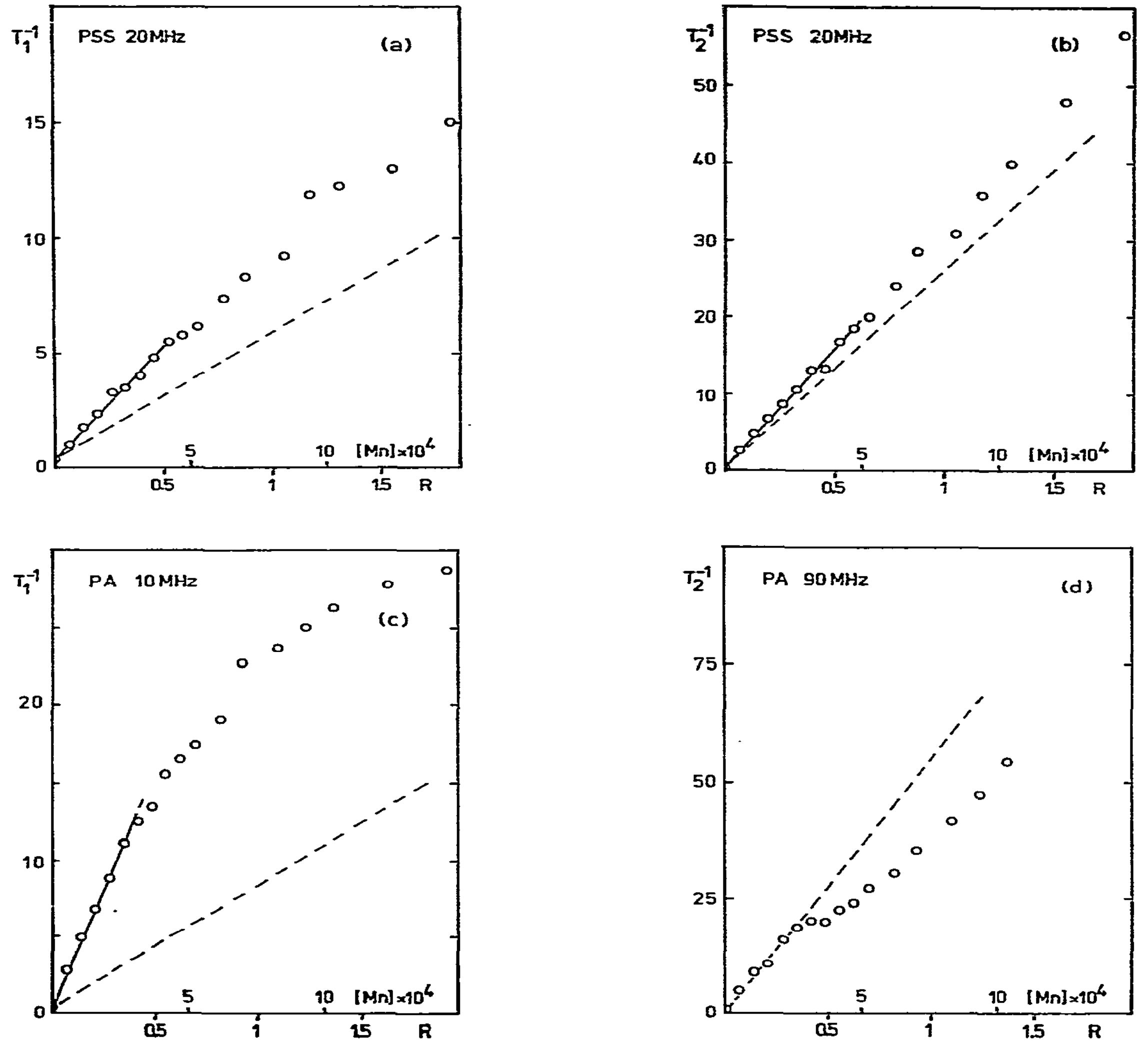


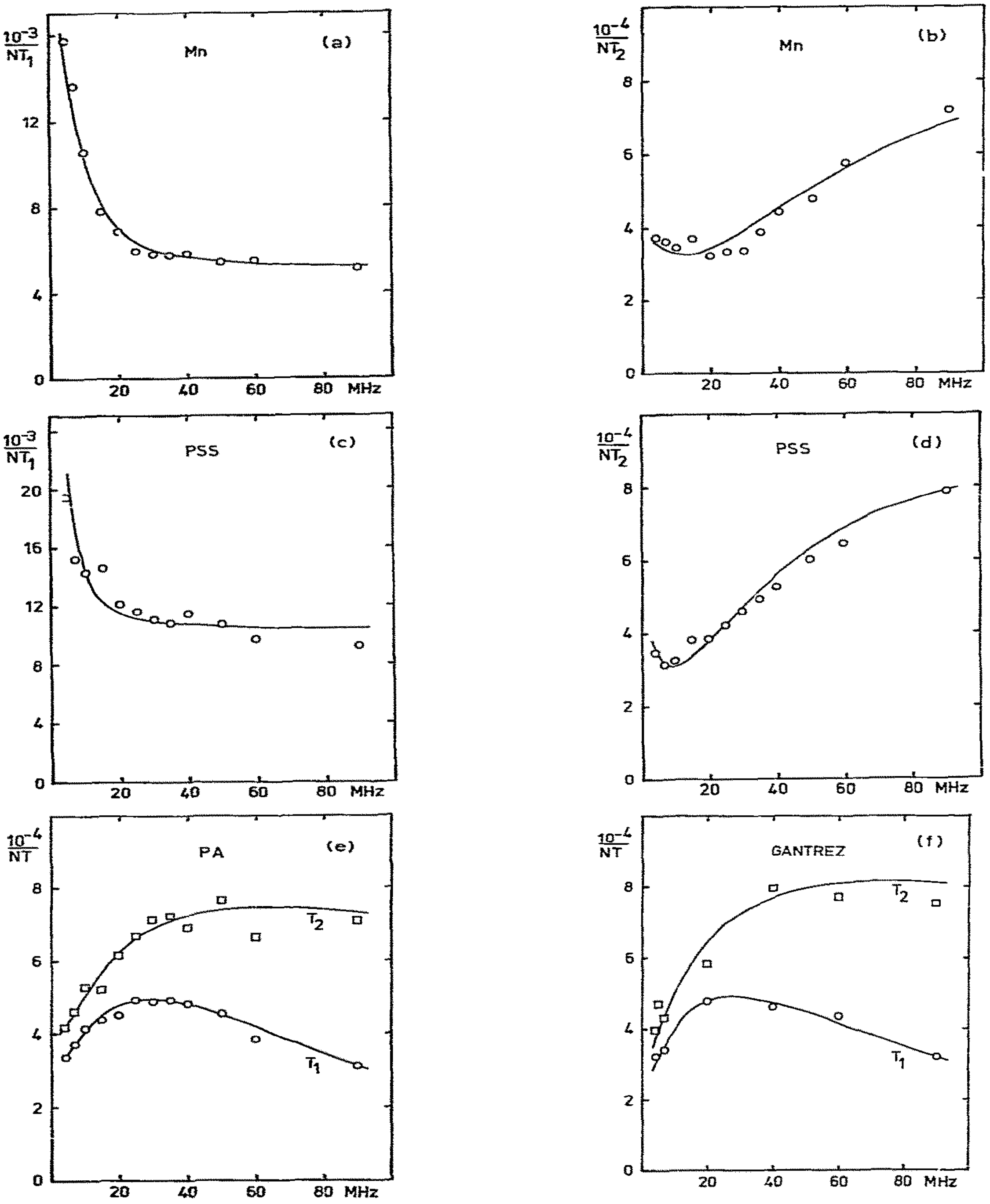
Fig. 2. Relaxation rates T_1^{-1} and T_2^{-1} (in s^{-1}) of water in the polyelectrolyte solution as a function of the concentration of added Mn^{2+}. The R scale gives the corresponding Mn^{2+}/polymer ratio. The dotted line gives the relaxation rates in the absence of polyelectrolyte. a) and b): with PSS (1.6×10^{-3} N); c) and d): with PA (1.5×10^{-3} N).

$$(NT_i)^{-1} = (T_{i\,\text{observed}}^{-1} - T_{iw}^{-1})/[\mathrm{Mn}^{2+}] = \frac{1}{55\,P_M T_i},$$

where T_{iw} is the bulk water relaxation time in the presence of polyelectrolyte with no Mn^{2+}, N the molarity and P_M the molar fraction of manganese ions.

Fig. 3 gives such a frequency dependence for Mn^{2+} alone and in the presence of the four polyelectrolytes.

It is qualitatively clear that for PSS — which from chemical shift experiment does'nt seem to induce any dehydration of Co^{2+} — the frequency dependence closely parallels that for Mn^{2+} alone. It is very dif-


(a)
Mn
$\frac{10^{-3}}{NT_1}$
0
4
8
12
20
40
60
80 MHz
(b)
Mn
$\frac{10^{-4}}{NT_2}$
0
2
4
6
8
20
40
60
80 MHz
(c)
PSS
$\frac{10^{-3}}{NT_1}$
0
4
8
12
16
20
20
40
60
80 MHz
(d)
PSS
$\frac{10^{-4}}{NT_2}$
0
2
4
6
8
20
40
60
80 MHz
(e)
PA
$\frac{10^{-4}}{NT}$
T_2
T_1
0
2
4
6
8
20
40
60
80 MHz
(f)
GANTREZ
$\frac{10^{-4}}{NT}$
T_2
T_1
0
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4
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60
80 MHz

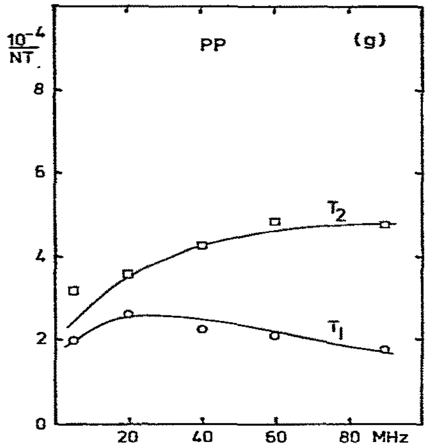


Fig. 3. Normalized relaxation rates $(NT_1)^{-1}$ and $(NT_2)^{-1}$ (for small values of R) as a function of frequency. In each figure the full curve represents the best fit obtained from relations (3) and (4). a) and b): Mn^{2+} in absence of polyelectrolyte; c) and d): in presence of PSS; e): in presence of PA; f): in presence of Gantrez; g): in presence of PP.

ferent for the three other polyelectrolytes. In all cases a detailed analysis is required to extract the hydration and mobility parameters.

3.3. EPR measurements

The fine structure of the Mn^{2+} ion cannot be observed any more at low R in polyphosphate and Gantrez [10]. It remains, however, clearly visible for PSS and PA. Each of the six lines results from five overlapping lines due to the zero field splitting [11]. The resulting line broadening is known to be minimal for the fourth line from low field and the change of its width reflects the change in the electron spin relaxation time τ_s [12]. These changes as a function of R are given in fig. 4.

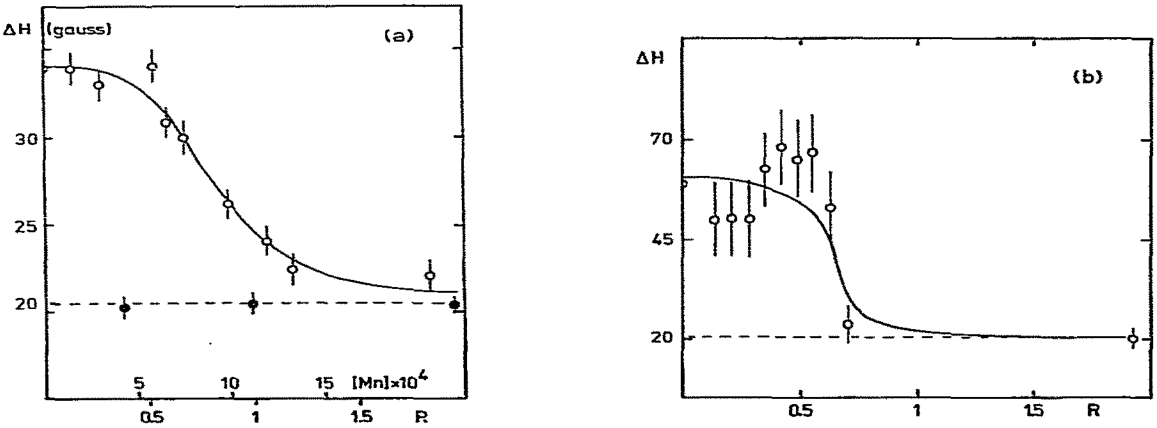


Fig. 4. Line width of the fourth line in the Mn^{2+} EPR spectrum as a function of R; dotted line: line width with no polyelectrolyte. a) for PSS; b) for PA.

4. Analysis and interpretation of the results

The chemical shift $\Delta\nu/\nu$ of water protons can arise from both the contact interaction resulting from the hyperfine coupling (A) and from the pseudo contact interaction resulting from an incomplete averaging of the dipolar interaction in the case of an anisotropic g factor of the paramagnetic ion. In the fast exchange limit, the chemical shift is given by [23]:

$$\frac{\Delta\nu}{\nu}\text{contact} = -P_M \frac{g\beta S(S+1)}{\gamma_H 3kT} qA, \tag{1}$$

$$\frac{\Delta\nu}{\nu}\text{pseudo contact} = P_M \beta^2 \frac{S(S+1)}{27kT}$$

$$\times (g_\parallel + 2g_\perp)(g_\parallel - g_\perp) q' \left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle_{q'} \tag{2}$$

where β is Bohr's magneton, S the electron spin, γ_H the proton magnetogyric ration, θ and r define the position of the proton with respect to the g tensor axis. The two last factors in relations (1) and (2) measure the overall contact or pseudo contact interaction in terms of the product of a number of water molecules by an hyperfine or geometric constant which have different ranges. For that reason q and q' have not been set formally equal.

The change in the slope $\Delta\nu/\nu$ as a function of P_M for Co^{2+} alone and in the presence of polyelectrolyte could then result from the superposition of any of the following effects:

i) the replacement of some water molecules (change in q with A constant)

ii) a possible change in the hyperfine constant A due to partial or complete release of the electrostriction

iii) a loss of symmetry in the environment of the paramagnetic ion leading to a pseudo contact shift.

It seems that i) has to take place before ii) and iii) contributes appreciably to the change in $\Delta\nu/\nu$. The formation of a close contact ion pair redistributes the charge and subsequently the electrostriction weakens or disappears. Binding of ligands breaks the symmetry and makes the g factor anisotropic.

The shift observed in TMA as a function of R can indeed be attributed to the existence of a pseudo contact shift. The fact that PSS, for which $\Delta\nu/\nu$ is unchanged, produces a small but significant effect may indicate that smaller distorsions due to local electric fields are sufficient to create some loss of symmetry. The effect cannot however result from the influence of the overall radial field of the polyelectrolyte taken as a smeared cylindrical distribution of charge. In that case the TMA shift would always have the same sign while we have shown it to be of opposite sign in the case of carboxymethylcellulose [8].

The significance of the number n defined precedently (table 1) has to be handled with care. It should not be taken as the number of water molecules not replaced by ligands in the first hydration shell. The fact that it is roughly proportional to the total volume change when passing from a TMA to a Co^{2+} salt [9] would simply mean that in a first approximation A is proportional to the electrostriction and goes to zero when it is completely released. It suggests also that pseudo contact interaction plays a minor role for the water protons. Complementary information is anticipated from the analysis of the frequency dependence of the relaxation times.

For dilute solutions in the fast exchange limit, the frequency dependence of the relaxation rates $1/NT_i$ can be analysed in term of the Solomon-Bloembergen relations for the relaxation of water in the presence of paramagnetic ions which are extensively discussed in ref. [7]:

$$\frac{55}{NT_1} = D\left(\frac{6\tau_c}{1+\omega_I^2\tau_c^2} + \frac{14\tau_c}{1+\omega_S^2\tau_c^2}\right) + C\frac{2\tau_e}{1+\omega_S^2\tau_e^2}, \tag{3}$$

$$\frac{55}{NT_2} = D\left(4\tau_c + \frac{3\tau_c}{1+\omega_I^2\tau_c^2} + \frac{13\tau_c}{1+\omega_S^2\tau_c^2}\right)$$

$$+ C\left(\frac{\tau_e}{1+\omega_S^2\tau_e^2} + \tau_e\right). \tag{4}$$

The scalar interaction of amplitude C is modulated with the correlation time τ_e resulting from both the electronic spin relaxation time τ_s and from the water exchange time τ_M;

$$C = qC_M = q\tfrac{2}{3}S(S+1)A^2, \tag{5}$$

$$\tau_e^{-1} = \tau_s^{-1} + \tau_M^{-1}. \tag{6}$$

The dipolar interaction of amplitude D is modulated with the correlation time τ_c which incorporates the rotational correlation time τ_R of the hydrated complex:

$$D = qD_M f = q\,\frac{1}{15}\,\frac{S(S+1)}{r^6}\,(\gamma_H g\beta)^2 \cdot f, \tag{7}$$

$$\tau_c^{-1} = \tau_R^{-1} + \tau_e^{-1}, \tag{8}$$

where f is a geometrical factor less than unity, which takes in account the anisotropy of motion of the vector between the electron and nuclear spins (see ref. [7] p. 187); ω_I and ω_S are the nuclear and electronic resonance frequencies at a given field H_0.

We have left out any contribution due to the modulation of the pseudo scalar interaction which can formally be considered [14] since the g tensor anisotropy is much smaller for Mn^{2+} (used in the relaxation experiments) than for Co^{2+} [20], and since it is the square of the interactions responsible of the shift which come into the formulae, making the ratio of pseudo contact to contact interaction surely negligible.

The application of these formulae to the case where the counterion can exchange between two different environments with different hydration might be questioned. Indeed, even if the population of one of the species is much bigger than the other, as expected for site binding at low R, the dynamic of the binding might introduce new terms in the spectral densities associated with the modulation of both the dipolar and the scalar interaction. Some information on the time scales involved can be in some cases obtained from the analysis of the dispersion of the ultrasonic absorption [21]. Since however, the Solomon-Bloembergen relations are already a function of five parameters C, D, τ_R, τ_M and τ_s there is little hope to develop useful expressions for more complicated models. Therefore we use these equations as the simplest phenomenological equations for the modulation of the dipolar and scalar interaction with average correlation times τ_c and τ_e and we shall discuss their possible meaning later on. One difficulty arises however, from the fact that the electronic spin relaxation τ_s is frequency dependent. τ_c will however be frequency independent if τ_s is much larger than τ_M or τ_R.

We shall use the approximate frequency dependence relation of Bloembergen and Morgan [13]:

$$\tau_s^{-1} = B\left(\frac{\tau_v}{1+\omega_S^2\tau_v^2} + \frac{4\tau_v}{1+4\omega_S^2\tau_v^2}\right), \tag{9}$$

where B is related to the zero field splitting which is modulated by the fluctuations in the symmetry of the environment with the correlation time τ_v.

A true mathematical fit of the experimental data to a six parameter expression through a multi parameter regression scheme would require, to be statistically valid, an impossible experimental accuracy. Moreover, we are dealing with two sets of theoretical relations and measurements for T_1 and T_2. They contain the same parameters and cannot be treated independently. Fortunately there are cases where some of the terms are negligible and an approximate value of some of the parameters can be estimated from the information obtained from the chemical shift and EPR experiments. We therefore describe successively the treatment of the data concerning the different polymers, at values of R corresponding to the first linear part according to three classes:

PSS:
- frequency dependence of T_1 and T_2 similar to free Mn
- no effect of polymer on chemical shift
- fine structure in the Mn^{2+} EPR spectrum

PA:
- frequency dependence of T_1 and T_2 different from free Mn
- some effect on chemical shift [8]
- fine structure in the Mn^{2+} EPR spectrum

Polyphosphate and Gantrez:
- frequency dependence of T_1 and T_2 different from free Mn
- the polymer completely inhibits the effect of Co^{2+} on the water protons chemical shift
- only a broad unresolved EPR signal.

1) Mn^{2+} and PSS

Considering the order of magnitude of τ_s deduced for free Mn^{2+} and PSS Mn from EPR line width at X band ($H_0 \sim 3600$ G, $\omega_I \sim 15$ MHz, $\tau_s \sim 2$–3×10^{-9} s) the constant value of T_1^{-1} at high ω_I and the higher values at low ω_I indicate that τ_c is dominated by τ_R. Neglecting at first the scalar term in T_1 the value at high ω_I gives directly the first term in relation (3) i.e. $6D\tau_c$ while the frequency dependence at low ω_I gives τ_c. One then calculates the dipolar contribution to T_2^{-1} and, after subtraction, the scalar

Table 2
Best fit parameters derived from the frequency dependence of the relaxation rates of water in presence of Mn^{2+}

Parameter	$\tau_R \times 10^{11}$ (s)	$\tau_M \times 10^{9}$ (s)	$\tau_v \times 10^{12}$ (s)	$D \times 10^{-13}$ (s^{-2} rad)	$C \times 10^{-12}$ (s^{-2} rad)	$B \times 10^{-18}$ (s^{-2} rad)
Our results	2.9 ± 0.3	1.8 ± 0.2	4.5 ± 0.5	3.1 ± 0.3	4.8 ± 0.5	8.2 ± 0.8
Previous results	3 [13] 5 [15]	2.3 [13] 3 [16]	1.6 [18] 2.1 [13] 2.4 [17] 4.6 [19] 5 [11]	3.24 [13]	4.8 [13]	10 [13]

contribution (see relation 4). For Free Mn^{2+}, C is known from other experiments, as the chemical shift of the proton in the hexahydrated ion [13]. The frequency dependence of τ_e^{-1} is then calculated and fitted to the three parameter equations (6) and (9). This first set of parameters is used to calculate the scalar contribution to T_1 and by subtraction a corrected dipolar contribution. Iteration is then carried on.

In that procedure D and τ_R are obtained to a very good accuracy. C is taken for PSS-Mn to be equal to that of free Mn^{2+} from the chemical shift result. The final set of values for Mn^{2+} is given in table 2 where the results obtained by other authors for Mn^{2+} have been reproduced for comparison. Corresponding values for PSS-Mn are given in table 4.

2) PA

The frequency dependence of T_1 suggests that τ_c cannot be taken as constant. Since, from EPR, τ_s (1.1×10^{-9} s) has not changed in order of magnitude this implies that τ_R has increased and is now of the same order of magnitude as τ_s making $\omega_s^2\tau_c^2 \gg 1$ in the whole frequency range. On the other hand the chemical shift indicates a decrease for C. We therefore start neglecting the scalar term in T_1 and reduce relation (3) to:

$$6D\tau_c/(1 + \omega_I^2\tau_c^2)$$

and as a first approximation to the value of D, we take:

$$D/D_{Mn^{2+}} = n/6,$$

where n is taken from table 1. The frequency dependence of τ_c is then fitted according to relations (5), (6) and (7) with the three parameters ($1/\tau_r + 1/\tau_M$), τ_v and B. The best fit curve gives smoothed values of τ_c at each frequency from which one recalculates the dipolar contribution to T_2 and by subtracting the scalar contribution. B and τ_v being given, its frequency variation is fitted with two parameters C (which should be close to $(n/6)C_{Mn^{2+}}$) and τ_M.

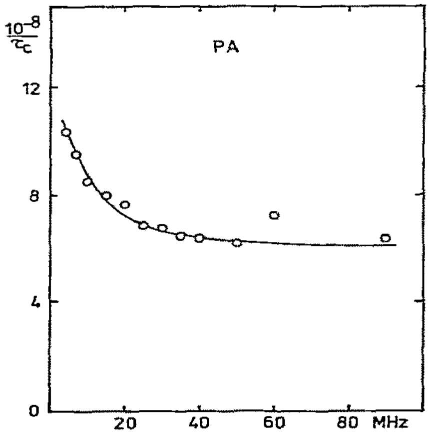


Fig. 5. Frequency dependence of τ_c^{-1} in the analysis of the relaxation rate of water in the presence of PA-Mn (low R). The full curve correspond to the fit according to equations (6), (8) and (9).

An example of the fit of $1/\tau_c$ as a function of ω is given in fig. 5. The changes in the calculated frequency dependences arising from the small changes in the parameters given in table 3 are depicted in fig. 6. They give an idea of the accuracy and justify in particular that the values of D and τ_R reported in table 4 are given to an accuracy of 10%.

3. Polyphosphate and Gantrez

From the chemical shift results, one would expect

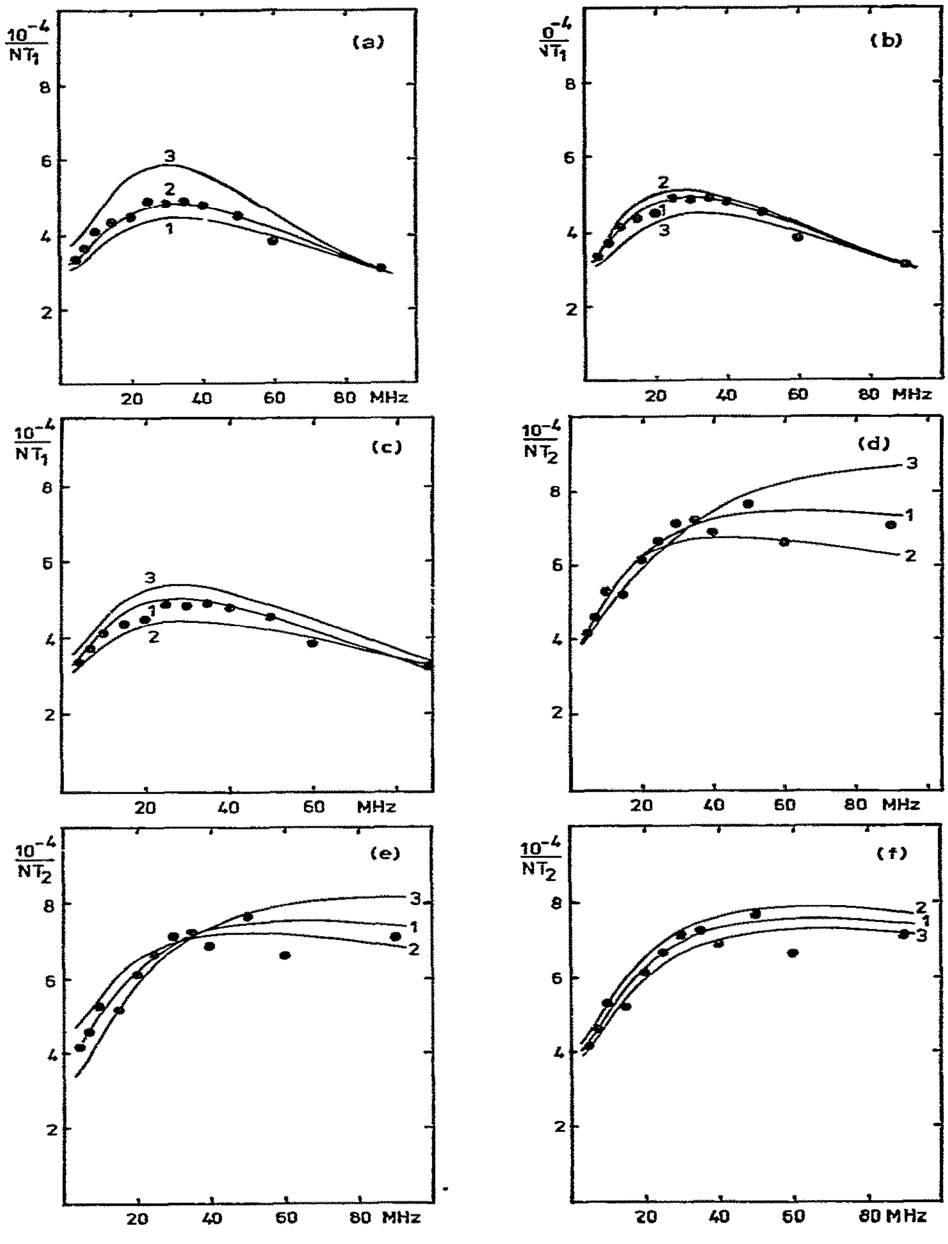


Fig. 6. Effect of small variations of the "best fit" parameters for the frequency dependence of the water relaxation rates in the presence of PA-Mn. The set of parameters correspond to table 3.

Table 3
Influence of small changes in the parameters on the fit of the frequency dependences: set of values used in fig. 6 for PA-Mn

Reference of the curve on fig. 6		$\tau_R \times 10^9$ (s)	$D \times 10^{-12}$ (rad.s^{-2})	$\tau_M \times 10^8$ (s)	$B \times 10^{-18}$ (rad.s^{-2})	$\tau_v \times 10^{11}$ (s)	$C \times 10^{-11}$ (rad.s^{-2})
(a)	1)	1.65	5.6	2.5	10.5	1.05	19
	2)	1.85	5.6	2.5	10.5	1.05	19
	3)	2.5	5.6	2.5	10.5	1.05	19
(b)	1)	1.8	5.9	2.5	8	1.3	9.7
and	2)	1.8	5.9	2.5	7	1.7	3.7
(d)	3)	1.65	5.9	2.5	10.5	1.05	19
(c)	1)	1.8	5.9	2.5	8	1.3	9.7
	2)	1.4	4.9	2.5	8	1.3	9.7
	3)	1.8	6.3	2.5	8	1.3	9.7
(e)	1)	1.8	6.9	2.5	8	1.3	9.7
	2)	1.8	6.9	2.5	5.33	1.3	6.47
	3)	1.8	6.9	2.5	8	1.3	9.7
(f)	1)	1.8	5.9	2.5	8	1.3	9.7
	2)	1.9	5.9	2.5	8	1.3	9.7
	3)	1.8	5.6	2.5	8	1.3	9.7

C to be close to zero and the expressions of T_1 and T_2 to be both reduced to their dipolar part. Then τ_c would be uniquely determined by the ratio of T_1 to T_2 and D obtained from the absolute values. τ_c varies in the range 10^{-8}–10^{-9} but D is not found constant, varying between 2×10^{11} and 3×10^{12} rad.s^{-2} for PP and between 6×10^{11} and 6×10^{12} rad.s^{-2} for Gantrez. Assuming this variation to be partly due to experimental inaccuracy in T_1/T_2, we have taken for D the value obtained at 90 MHz, where the sensitivity and stability are best, and we have recalculated the frequency dependence of τ_c and the values of T_2. The agreement is never very satisfactory and is very much improved by adding a small scalar contribution. The iterative process is then the same as for PA. The "best fit" parameters from which full curves of fig. 5 have been drawn are given in table 4.

5. Discussion of the results

The parameters of table 4 can now be discussed in terms of hydration and mobility of the counterion. The relaxation study on PSS nicely confirms the chemical shift data. The fact that D is the same as for free Mn^{2+} implies the same number of water mole-

Table 4
Best fit parameters from the frequency dependence of the relaxation rates of water in the presence of Mn salts, according to relations (3) to (7)

Parameters	Free Mn^{2+}	PSS-Mn	PA-Mn	Gantrez-Mn	PP-Mn
$\tau_R \times 10^{11}$ (s)	2.8 ± 0.3	5.7 ± 0.6	(1.8 ± 0.2) × 10^2	(1.6 ± 0.3) × 10^2	(1.6 ± 0.5) × 10^2
$\tau_M \times 10^8$ (s)	1.8 ± 0.2	1.8 ± 0.2	2.5 ± 0.8	3.5 ± 1.3	~5
$\tau_v \times 10^{11}$ (s)	0.45 ± 0.05	0.85 ± 0.09	1.3 ± 0.3	~2	~7
$D \times 10^{-12}$ (s^{-2} rad)	31 ± 3	31 ± 3	5.9 ± 0.6	6.1 ± 1.2	3.2 ± 1
$C \times 10^{-12}$ (s^{-2} rad)	4.8 ± 0.5	4.8 ± 0.5	0.9 ± 0.3	1 ± 0.4	~0.5
$N \times 10^{-18}$ (s^{-2} rad)	8.2 ± 0.8	8.2 ± 0.8	8 ± 2	8 ± 4	~8

cules in the first hydration shell. The rotational correlation time τ_R is however twice that for free Mn^{2+}. This can be interpreted in terms of a "local viscosity" in agreement with the fact that τ_v, the correlation time for the modulation of the zero field splitting by solvent collisions, is also about twice that for pure Mn^{2+}. The values of τ_s calculated from formula (7) at the EPR frequency using B and τ_v of Table 4 are 6.8×10^{-9} s for Mn^{2+} and 5.3×10^{-9} s for PSS-Mn, systematically higher than the values deduced from EPR line widths. This has been already noted [16] and attributed to:

– the non-lorentzian EPR line shape which results from the overlap of several transitions,

– the oversimplification contained in the relations (5) and (6) where no distinction is made between the longitudinal and transversal electronic relaxation times τ_{1s} and τ_{2s},

– the oversimplification of relation (9) as compared with more exact calculations.

For PA, PP and Gantrez, the qualitative similarity in the shape of the frequency dependence of $(NT_1)^{-1}$ and $(NT_2)^{-1}$ comes from the fact that τ_c becomes of the order of magnitude of τ_c and partly reflects its frequency dependence.

In the case of PA, EPR experiments reveal that τ_s has not much changed compared to the free Mn^{2+} value and therefore the analysis performed to extract τ_R and D seem very reliable considering the effect of small changes in the "best fit" parameters depicted in fig. 6. If we compare the relative amplitudes of the dipolar and scalar interactions for PA-Mn and Mn^{2+} with no polyelectrolyte we find $D/D_{Mn^{2+}} \sim C/C_{Mn^{2+}} \sim 0.2$. This result is in good agreement with the value $n/6 \sim 0.25$ where n is the apparent hydration number derived from chemical shift data (table 1).

The value of the remaining dipolar interaction requires further discussion. Indeed, if $C/C_{Mn^{2+}}$ reflects the loss of hyperfine interaction resulting from both the replacement of some water molecules by ligands from the polymer and the subsequent relaxation of the electrostriction on the remaining water molecules, one would expect $D/D_{Mn^{2+}}$ to reflect mainly the replacement of water molecules since a slight increase of the ion-water protons distance has only a small influence on the dipolar interaction. One should therefore postulate the replacement of a least 4 molecules of water. Such a strong binding seems contradictory with the value of $\tau_R \sim 10^{-9}$ s, unless it reflects the local and highly anisotropic motion of the polymer chain. In that case the anisotropy factor f should be much smaller than unity indicating a smaller replacement of water by ligands. The number of water molecules replaced in the first hydration shell upon site binding cannot therefore be unambiguously determined. The two order of magnitude increase in τ_R can however be taken as a good criterion for site binding together with the decrease in the amplitude of the scalar interaction.

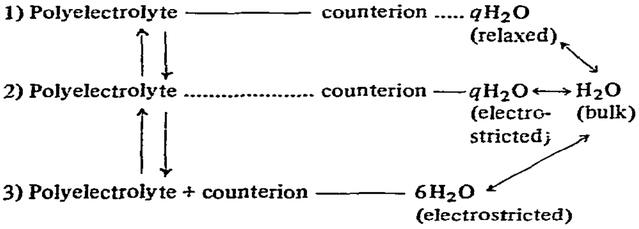
The situation for PP and Gantrez is somewhat more complicated. While the EPR line width suggest a large decrease in the transverse electron spin relaxation time, the fitting of the frequency dependence of τ_c and of the residual scalar interaction leads to values of B and τ_v which imply only a small increase in τ_s. This makes the use of formulae (3) and (4), in which no distinction is made between the transverse and longitudinal values of τ_s, more questionable. Even if one neglects completely the scalar interaction the values of τ_c remain in the range 10^{-8}–10^{-9} s and therefore none of the correlation times τ_R, τ_M or τ_s can have a much smaller value; once again the large increase in τ_R appears as the reliable test of site binding.

In fact τ_R could in that case be much longer. The scalar contribution would then be very small at the highest frequency and the values of $D/D_{Mn^{2+}}$ and τ_c obtained at 90 MHz are therefore quite reliable. These values ($D/D_{Mn^{2+}} \sim 0.1$–0.2) are similar to that obtained for PA. On the other hand, the apparent discrepancy between the amplitude of the scalar interaction revealed by shift and relaxation measurements can be due to the crudeness of relation (9) and the absence of distinction between the longitudinal and transverse electron spin relaxation time.

A tentative model can be proposed out of our results. Site binding is characterized by the replacement of one or two molecules of water in the first hydration shell by ionized groups from the polymer with formation of a close contact ion pair. The subsequent relaxation of the electrostriction has a very large effect on the decrease of the counterion paramagnetic spin—water proton nuclear spin hyperfine interaction, justifying the parallelism of the shift and volumetric results. The apparent decrease of the dipolar interaction reflects the anisotropy of the motion of the partly hydrated site bound counterion, controlled by the local conformational changes of the polymer backbone.

In that picture, the residence time of the site bound counterion must be much longer than the measured correlation time τ_R. Ultrasonic dispersion data on PP-Co [21] reveal however that the binding proceeds according to a three step model. Each intermediate state is characterized by different states of hydration corresponding in particular to the outer sphere and inner sphere complex in fast exchange. Each intermediate state would then be characterized by a different value of C and D and the spectral densities would result from the modulation by exchange. This could explain a negligible contribution of the scalar interaction in the static shift experiments, related to a high population of the inner sphere complex, while the modulation of this scalar interaction in the exchange with a small amount of outer sphere complex could noticeably affect the relaxation.

In the case of a two step model, the Solomon-Bloembergen relations might remain a phenomenological approximation with a redefinition of τ_R and τ_M. The analysis is hopeless for a larger number of parameters as requested in a three step model of the type given below:



We have only one indication suggesting that exchange between states of different hydration might control the relaxation. This comes from a consideration of the relaxation time associated with the "atmospherically trapped" counterions. Indeed in the case of PA, the break in the $1/T_1$ and $1/T_2$ curves as a function of R is sufficiently clear to define, by subtraction of the counterion of the site bound counterions, the relaxation rates for the second type of condensed counterions. One would expect their frequency dependence to resemble that found in the case of PSS. They in fact closely resemble that found for PA at low R, i.e. in the case of site binding.

Our attempt to quantitatively analyze the change in relaxation time of water under the influence of Mn^{2+} in the presence of polyelectrolyte in terms of hydration and mobility appears therefore more complicated than anticipated. However, using the Solomon-Bloembergen relations as a phenomenological approach, the decrease in D and C and the increase in τ_R appear as reliable signs of site binding.

It is difficult to discuss at that stage the reason why, among polymer with the same charge per unit length PSS does not produces site binding and why in the other cases only a fraction of the condensed counterions is able to site bind. In a simple picture, initially introduced by Eisenmann [22] to explain the specificity of binding of alkaline ions to different anions, site binding would be controlled by the strength of the local electric field. It governs the balance between the change in free energy resulting from the modification in the structure of the hydration sphere and the change in electrostatic energy resulting from a closer contact allowed by that modification. The problem in the case of polyelectrolytes is to decide whether the major contribution to the local electric field arises from the nearest ionized group or from the overall charge distribution along the polyelectrolyte. If the second hypothesis holds, it will at the same time explain the limitation in the number of binding sites. The first site bound counterions decrease the charge per unit length up to the point where the electric field is not high enough to permit further site binding. Another limitation could however proceed from a conformational constraint for ligand exchange with divalent counterions.

Some arguments can be found in our results in favor of a control of site binding by the overall field of the polyelectrolyte. This field depends not only of the charge by unit length but of the distance of the charged site groups from the main chain. It is also known that the volume change on divalent cation addition, which is very small for PSS, is much larger for polyethylene sulfonic acid where the same SO_3^- group is closer to the main chain [4];

Polyacrylic acid offers a way to test this hypothesis by performing chemical shift and relaxation experiments at variable degrees of ionization. These experiments are now under way.

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