

^{23}Na Nuclear Magnetic Resonance in Polyanion Solution. Correlation Times and Quadrupole Coupling Constants of Na^+ Bound to Poly(methacrylic acid)

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Abstract: The information obtained on the interaction between small ions and polyions from studies of an ion's quadrupole relaxation is examined in some detail. Important features usually found in the NMR studies of polyelectrolyte systems are inequality of the longitudinal (T_1) and transverse (T_2) relaxation times, relaxation given by the sum of two exponential decays, and a non-Lorentzian resonance signal. The utilization of these features to deduce the correlation time of the polymer-bound counterion is described as well as the estimation of the quadrupole coupling constant. An illustration of the principles developed is given by the system Na^+ -poly(methacrylic acid), for which detailed experimental data are presented. The analysis gives a description in terms of the correlation times, quadrupole coupling constants, and degree of counterion binding. The correlation time is found to increase strongly with decreasing degree of ionization and this is attributed to a conformational transition. An increase in the quadrupole coupling constant at low ionization degrees is suggested to be due to the involvement of both carboxylate and carboxylic acid groups in the ion binding, and this is supported by $^{23}\text{Na}^+$ chemical shifts. The results are compared with those of the system Na^+ -poly(acrylic acid) and marked differences are found between the two polyanions.

Introduction

In biological systems, the interaction between charged macromolecules and their surrounding ionic media is of great importance. A good understanding of the nature of these interactions is a prerequisite for an understanding, on a molecular level, of the biological functions. Various NMR parameters have been shown to offer a means for a detailed investigation of the interactions between small ions and biological macromolecules.¹ Our preliminary investigations of, e.g., mucopolysaccharides with ^{23}Na NMR have, in some cases, revealed very complex interaction patterns.^{2,3} This has led us to investigations of simpler model systems to gain a better basis for interpreting the fundamental modes of ionic interactions occurring in polyelectrolyte systems.

This report treats the $^{23}\text{Na}^+$ NMR relaxation rates and chemical shifts of aqueous poly(methacrylic acid) and poly(acrylic acid) solutions under various experimental conditions. These synthetic polyanions have been studied by other physicochemical methods by several workers.⁴⁻⁶ As will be demonstrated for these relatively simple systems (compared to most biosubstances), rather detailed considerations are also required in the interpretations of the NMR parameters. In particular the effect of nonexponential relaxation in the analysis of various relaxation experiments is outlined. The analysis leads to values of the quadrupole coupling constant and the correlation time of bound Na^+ ions at various degrees of ionization of the polyion. The use of these quantities as well as the NMR shielding for certain aspects of polyion-counterion interactions is briefly outlined, while a detailed discussion in chemical terms comparing different polyelectrolyte structures, charged groups, and counterions is deferred to a later publication.

Experimental Section

The poly(acrylic acid) (PAA), bought as a 25% aqueous solution from British Drug Houses Ltd., was titrated with NaOH and diluted with distilled water to obtain slightly alkaline sodium-PAA solutions of desired concentrations. Such solutions were used in the NMR and pH-titration experiments without further purification.

The synthesis of the poly(methacrylic acid) (PMA) used has been previously described.⁷ The degree of neutralization, α , was determined from pH-titration curves. In the NMR experiments as well as for the pH titrations, α was varied by adding concentrated (ca. 9 M) aqueous HCl to the PMA and PAA solutions. The volume changes in these

titrations are less than 5% and can, for our purposes, be disregarded. This procedure was used to obtain a constant ratio of total concentration of polymer to total sodium. In one case, PMA was titrated to $\alpha = 0.8$ with NaOH and then titrated back with HCl during the NMR measurements.

The $^{23}\text{Na}^+$ line widths and chemical shifts were determined on a modified Varian XL-100 spectrometer, operating in the FT mode at 26.46 MHz, in the same way as has been described in ref 7. The definition of the chemical shift used here is that a downfield shift is positive. The longitudinal (T_1) and transverse (T_2) relaxation times were measured using a Bruker BK 322-s spectrometer operating at 23.81 MHz, equipped with a Varian 71 computer (for data processing) and an external proton field lock. The time variation of the longitudinal magnetization was recorded after 180- τ -90 pulse sequences for six different delay times. To improve both accuracy and sensitivity in the individual measurements, integrals of part of the free induction decay curves were used as measures of magnetization for the different delay times. T_1 values were obtained according to a linear least-squares fit of the logarithm of magnetization vs. time. As a test of the accuracy of the individual measurements, four integration areas over the free induction decay were used. The relaxation rates thus found were well within 3% of the average value. The reported T_2 values were obtained from the transverse magnetization from a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. The computer-programmed analysis of the magnetization data is a least-squares fit to a single exponential with the fit being terminated when the magnetization reached 20% of its value at the first echo. The relaxation times are the average of at least two separate determinations. The experimental errors in the individual measurements are estimated to be less than 4% in both T_1 and T_2 . The temperature during all NMR experiments was 29 ± 1 °C.

Theory

For the reader's convenience we give a collection of the NMR quadrupole relaxation equations which have a direct bearing on the present study. $^{23}\text{Na}^+$ is a quadrupole nucleus with spin quantum number $I = 3/2$. Its relaxation is mainly (in the absence of paramagnetic species) due to interactions between its quadrupole moment and the time varying electric field gradients at the place of the nucleus. It has been demonstrated⁸ that the time dependence of the magnetization in a system where the relaxation is dominated by quadrupole relaxation cannot, in general, be described by a single exponential for the transverse and longitudinal magnetization of a nucleus with $I > 1$.

The quadrupolar relaxation equations for a spin $3/2$ nucleus involved in chemical exchange have been derived elsewhere.⁹

For rapid, two-site exchange, the longitudinal magnetization is

$$M_L(t) - M_{L,0} = (M_L(0) - M_{L,0}) \times (0.2 \exp(-a_1 t) + 0.8 \exp(-a_2 t)) \quad (1)$$

and the transverse magnetization in a coordinate system rotating at the resonance frequency is

$$M_T(t) = M_T(0)(0.6 \exp(-b_1 t) + 0.4 \exp(-b_2 t)) \quad (2)$$

where

$$a_1 = p_F R_F + p_B / T_{1,\text{fast}} \quad (3a)$$

$$a_2 = p_F R_F + p_B / T_{1,\text{slow}} \quad (3b)$$

$$b_1 = p_F R_F + p_B / T_{2,\text{fast}} \quad (4a)$$

$$b_2 = p_F R_F + p_B / T_{2,\text{slow}} \quad (4b)$$

Here p_F and p_B are the probabilities (which equal the mole fractions) of finding the nuclei in the free state (i.e., in aqueous solution) and in the bound state, respectively, R_F is the relaxation rate in the free state, and, finally,

$$1/T_{1,\text{slow}} = \frac{2\pi^2}{5} \chi^2 \tau_c / (1 + 4\omega^2 \tau_c^2) \quad (5a)$$

$$1/T_{1,\text{fast}} = \frac{2\pi^2}{5} \chi^2 \tau_c / (1 + \omega^2 \tau_c^2) \quad (5b)$$

$$1/T_{2,\text{fast}} = \frac{\pi^2}{5} \chi^2 \tau_c (1 + 1/(1 + \omega^2 \tau_c^2)) \quad (6a)$$

$$1/T_{2,\text{slow}} = \frac{\pi^2}{5} \chi^2 \tau_c (1/(1 + 4\omega^2 \tau_c^2) + 1/(1 + \omega^2 \tau_c^2)) \quad (6b)$$

In eq 5a-6b, χ is the quadrupole coupling constant, τ_c is the correlation time for the bound ions, and ω is the resonance frequency (in radians/s). If $\omega\tau_c$ is sufficiently small (in practice < 1.5), then eq 1 and 2 are approximately exponential with the appropriate time constants⁹

$$R_1 = p_F R_F + p_B \left(0.2 \frac{1}{T_{1,\text{fast}}} + 0.8 \frac{1}{T_{1,\text{slow}}} \right) \quad (7)$$

$$R_2 = p_F R_F + p_B \left(0.6 \frac{1}{T_{2,\text{fast}}} + 0.4 \frac{1}{T_{2,\text{slow}}} \right) \quad (8)$$

where $R_1 (= 1/T_1)$ and $R_2 (= 1/T_2)$ are the longitudinal and transverse relaxation rates, respectively. If $\omega\tau_c \ll 1$, the so-called extreme narrowing limit, then eq 7 and 8 give

$$R_1 = R_2 = p_F R_F + p_B \frac{2\pi^2}{5} \chi^2 \tau_c \quad (9)$$

(It has been demonstrated^{10,11} that the extreme narrowing condition normally applies in aqueous solutions of simple electrolytes.)

Finally, the high-resolution spectrum can be obtained by taking the Fourier transform of eq 2. The result is the superposition of two Lorentzians with the same resonance frequency but with line widths corresponding to the two relaxation rates b_1 and b_2 .

Clearly, if $\omega\tau_c$ is not too small, then there are at least three ways to determine the correlation time. By performing a fit of the transverse relaxation to two exponentials or by fitting the high-resolution spectrum to two Lorentzians, we can extract the two rate constants b_1 and b_2 . If $p_F R_F$ is known, then by subtracting this quantity from each of the rate constants we

can calculate

$$\Delta(R_2) = \left(\frac{R_{2,\text{fast}}}{R_{2,\text{slow}}} \right) = \frac{b_1 - p_F R_F}{b_2 - p_F R_F} = \frac{1 + 1/(1 + \omega^2 \tau_c^2)}{1/(1 + \omega^2 \tau_c^2) + 1/(1 + 4\omega^2 \tau_c^2)} \quad (10)$$

which is a function only of $\omega\tau_c$. Similarly, one can use the approximate relaxation rates in eq 7 and 8 to calculate

$$\Delta(T_2/T_1) = \frac{R_1 - p_F R_F}{R_2 - p_F R_F} = \frac{1.6}{1 + 4\omega^2 \tau_c^2} + \frac{0.4}{1 + \omega^2 \tau_c^2} = \frac{0.6 + \frac{0.4}{1 + 4\omega^2 \tau_c^2} + \frac{1}{1 + \omega^2 \tau_c^2}}{1 + 4\omega^2 \tau_c^2} \quad (11)$$

which is also a function only of $\omega\tau_c$. Once the correlation time has been calculated via eq 10 or 11, one can use this value in the other equations to calculate a value for $p_B \chi^2$ and thus the quadrupole coupling constant. For the evaluation of the quadrupole coupling constant, one has to have rather accurate independent information on p_B , to claim significance in χ . (At least for many polyelectrolyte systems it is probably an oversimplification to only consider one type of bound counterions. In this initial application it has not been considered worthwhile to go beyond the two-site model which will serve well for outlining the general methodology. In principle the extension is straightforward and will be made when more detailed data at varying counterion-polyion molar ratios are available.)

The counterion binding to polyelectrolytes cannot generally be discussed in terms of simple independent binding sites. More general models have been extensively treated in recent modern polyelectrolyte theory.¹²⁻¹⁴ An approximative model for polyelectrolyte-counterion interactions, originally proposed by Imai et al.^{15,16} and developed by Manning,^{17,18} is the so-called counterion condensation model. The parameters of main importance for binding of small ions to a highly charged polyelectrolyte ion are, in this model, the charge of the counterions and the charge per unit length (the charge density) on the polyion. Thus, it provides a model for nonspecific ionic interactions. It seems reasonable to use this model as a starting point for the evaluation of the amount of bound counterions. For more accurate estimates, effects of the special structures of both polyions and counterions also have to be considered.

Results and Discussion

Poly(acrylic acid). Van der Klink et al.¹⁹ have studied the ^{23}Na NMR longitudinal relaxation rate for aqueous solutions of poly(acrylic acid) (PAA) at various degrees of neutralization. In order to explain the observed relaxation behavior they attempted to apply the most commonly used polyelectrolyte model, i.e., the polyion was considered as a rather rigid rod with the charges smeared out continuously along the rod. This might be an acceptable model for a general view of counterion binding, but for the NMR relaxation of the "nearsighted" quadrupole nuclei, it will probably be misleading. For example, the distance between adjacent polyion charges even for α close to 1 is not much smaller than the distance for the closest approach of the counterions to the polyelectrolyte chain. Furthermore, in the discussion regarding the quadrupole relaxation mechanism in ref 19, it was assumed that the only molecular motion causing relaxation is the fast diffusion of sodium ions around the charged rod. This fast motion would average out only part²⁰ of the quadrupole interaction. Thus, the counterions should still experience an anisotropic environment and static quadrupole effects ought to be observable. Such effects are not observed. Therefore one has also to consider another motion, which averages out the rest of the quadrupole interaction. Since

the fast translational motion of counterions along the rod does not (in this model) produce any variation in the electric field gradient, we are left with the slow motions possible in the system. These would give the major contribution to the relaxation. The slow tumbling of the rod and the exchange of counterions with the bulk solution are examples of such motions.

It may be estimated that the reorientation time of the polyelectrolyte rod is so long that the extreme narrowing condition $\omega\tau_c \ll 1$ for relaxation should no longer apply.^{19,23} The data presented in Figure 1 show that the longitudinal and transverse relaxation times are almost equal. The slight difference observed (which corresponds to a correlation time of less than 0.5 ns) is, in fact, within the experimental error limits, and T_1 and T_2 can be considered equal. Therefore, it seems that the correlation time is not determined by the reorientation of the rigid polyion in the PAA solutions.

A more realistic model for relaxation is perhaps a flexible chain with point charges. Then a (fast) counterion motion along a curved rod and/or fast internal motions in the rod would be sufficient to explain the relaxation. An alternative possibility is that the lifetime of the Na^+ ion at the polyion is so short that the exchange dominates the correlation time.

Since we have not found any evidence for an inequality of T_1 and T_2 we may only say that for the PAA solutions at least one of the motions mentioned (counterion exchange, change of direction of the polyion segments, and counterion diffusion along a curved polyion rod) is faster than 0.5 ns. Further $^{23}\text{Na}^+$ relaxation studies are planned under conditions more suitable for obtaining the nonextreme narrowing situation, i.e., low temperature, higher magnetic field, and D_2O as solvent. In connection with the PAA results, it should be mentioned that, although not obtained under identical conditions, our $^{23}\text{Na}^+$ relaxation results parallel those of van der Klink et al.¹⁹ closely.

Included in Figure 1 are also the ^{23}Na NMR chemical shifts, δ , obtained for a similar PAA solution. An attempt has been made to use the concept of "counterion condensation" to explain the counterion binding in PAA.²¹ For the interpretation of the chemical shift data such a counterion condensation model might be acceptable since the rapid increase in δ starts at an α of about 0.4. (The high α value at the beginning of the increase in chemical shift can be explained by the presence of some methyl ester groups on the PAA which would cause a lowering of the charge density as compared to a fully dehydrated PAA.)

Chemical shift changes of ^{23}Na are dominated by changes in the paramagnetic shielding term. For monoatomic ions, chemical shifts are generally discussed in terms of the Kondo-Yamashita overlap model according to which the shielding may be schematically written²²

$$\sigma_p = -\frac{4\mu_B^2 \cdot \mu_0}{\pi \Delta E} \langle r^{-3} \rangle_p (A_{M-M} + A_{M-X} + A_{M-W})$$

where μ_B is the Bohr magneton, ΔE an average excitation energy, and $\langle r^{-3} \rangle_p$ the expectation value of r^{-3} for an outer p electron of the sodium ion. The A 's are overlap integrals between the outer p orbitals of the alkali ion (M) and the orbitals of other cations, anions (X), or water molecules (W).

The chemical shifts being dominated by short-range overlap effects should, in the absence of specific complex formation involving several groups on the polyion, vary with the degree of ionization in parallel with the number of counterions bound. From a counterion condensation two-site model essentially zero chemical shifts are expected until α corresponds to the critical charge density, and thereafter a linear increase in the shift to fully neutralized PAA would obtain. However, from the relaxation rates, it seems that additional binding is also present,

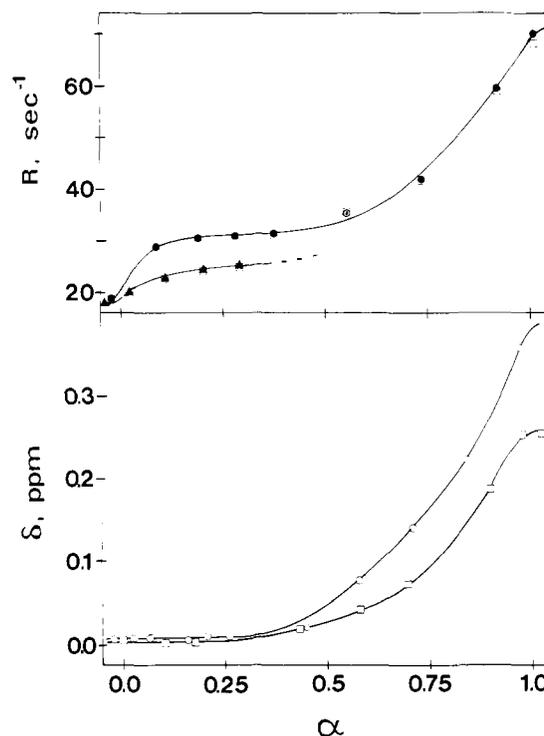


Figure 1. ^{23}Na relaxation rates, R (s^{-1}), and chemical shift, δ (ppm), as a function of the degree of neutralization, α , for four different aqueous poly(acrylic acid) solutions. The transverse relaxation rates presented are valid for the two PAA concentrations 0.64 (●) and 0.32 m (▲), with the total sodium ion concentration of 0.66 and 0.33 m , respectively. The longitudinal relaxation rates are for both cases given by the open squares (□). The lower part of the figure shows the variation of the ^{23}Na chemical shift for the two concentrations of PAA, 0.88 (□) and 0.25 m (○), with the sodium ion concentrations 0.11 and 0.30 m , respectively.

since nonzero contributions are observed also at low α . (The nearly zero chemical shifts observed at low α do not necessarily exclude binding; cf. discussion on PMA below.)

Poly(methacrylic acid). The relaxation pattern in PMA solutions is quite different from that observed in PAA solutions. In a previous study,⁷ we demonstrated that the ^{23}Na NMR line widths exhibit a marked maximum around a neutralization degree of 0.2. It was also observed that the relative height of the relaxation maximum is strongly enhanced when the PMA concentration is increased. To analyze the relaxation behavior in terms of the fundamental parameters determining relaxation, determinations of both T_1 and T_2 were performed. In Figure 2, the longitudinal (R_1) and transverse (R_2) relaxation rates, determined as described above, are presented as a function of α . For comparison the relaxation rates obtained from line widths, $\pi\Delta\nu_{1/2}$, are also included in the same figure. Three features of special interest are exhibited, namely, (1) maxima in both R_1 and R_2 are observed in the region around $\alpha = 0.2$, (2) there is a pronounced difference between R_1 and R_2 in the same α region, and (3) there is a difference between R_2 and $\pi\Delta\nu_{1/2}$, especially in the region $0.1 < \alpha < 0.3$.

As has been previously discussed,⁷ the increased relaxation around $\alpha = 0.2$ can be accounted for by a change in polyion conformation or another process affecting τ_c and/or a change in the nature or the amount of counterion binding. A change in counterion binding would affect the factor $p_B X^2$ in the expression for the relaxation rate. As may be inferred from eq 11 of the theoretical section, a dissimilar variation of R_1 and R_2 implies a variation in the correlation time for the bound ions.

Normally, one expects the transverse relaxation rate values to coincide with the relaxation rates obtained from line widths ($\pi\Delta\nu_{1/2}$). But this is strictly true only when τ_c is so short that

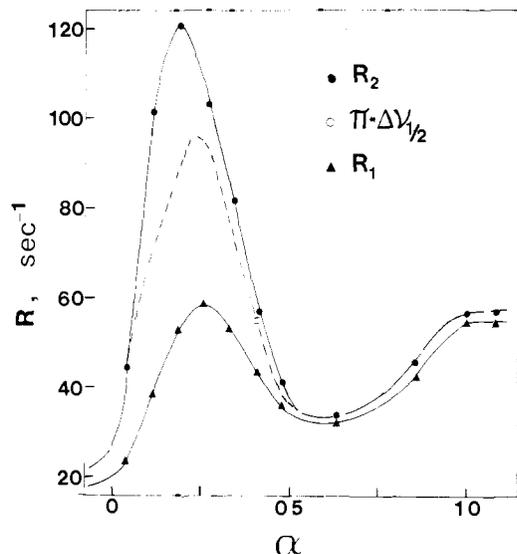


Figure 2. ^{23}Na relaxation rates in s^{-1} for a 0.47 *m* aqueous PMA solution as a function of α . The longitudinal, R_1 , and transverse, R_2 , relaxation rates are recorded at 23.81 MHz and the relaxation rate obtained from the line width, $\pi\Delta\nu_{1/2}$, at 26.46 MHz. The sodium ion concentration is 0.48 *m*.

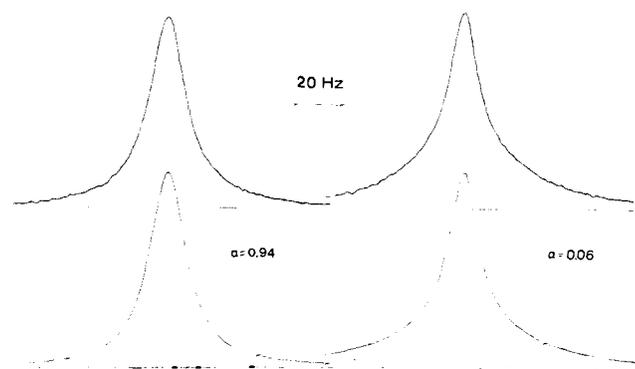


Figure 3. Experimental (upper) and theoretical (lower) ^{23}Na absorption spectra for 0.47 *m* aqueous PMA at $\alpha = 0.94$ (left) and $\alpha = 0.06$ (right). The theoretical curves are for $\alpha = 0.94$ a Lorentzian line with $1/T_2 = \pi\Delta\nu_{1/2} = 55.0 \text{ s}^{-1}$ and for $\alpha = 0.06$ the weighted sum of two Lorentzian lines with $R_{2,\text{fast}} = 180 \text{ s}^{-1}$ and $R_{2,\text{slow}} = 42 \text{ s}^{-1}$.

$\omega\tau_c \ll 1$ (i.e., under extreme narrowing conditions, where also $R_1 = R_2$). It is also a good approximation when the difference between R_1 and R_2 is not too big. When $\omega\tau_c$ becomes close to 1, an entirely different situation occurs. Then the transverse magnetization giving R_2 and $\pi\Delta\nu_{1/2}$ is no longer decaying exponentially, but rather by the sum of two exponentials as is shown in the general eq 2 in the Theory section. When the fast-decaying and the slow-decaying components are sufficiently different one will, in a line width measurement, obtain a value closer to the slow component than to the weighted mean of them. On the other hand, for a T_2 measurement performed as described in the Experimental Section, the fast component is given a larger weight. This explains qualitatively the observations presented in Figure 2.

Furthermore, if the difference between the relaxation components is very large, the broad component in the absorption spectrum is "hidden" in the baseline. The line width then measures only the narrow (= slow relaxing) component and only 40% of the total intensity is observed. For the T_2 determination, if the fast-relaxing component decays on a time scale comparable to the "dead time" of the spectrometer, mainly the slow component is left when the recording of the magnetization starts. Therefore, also with this method only

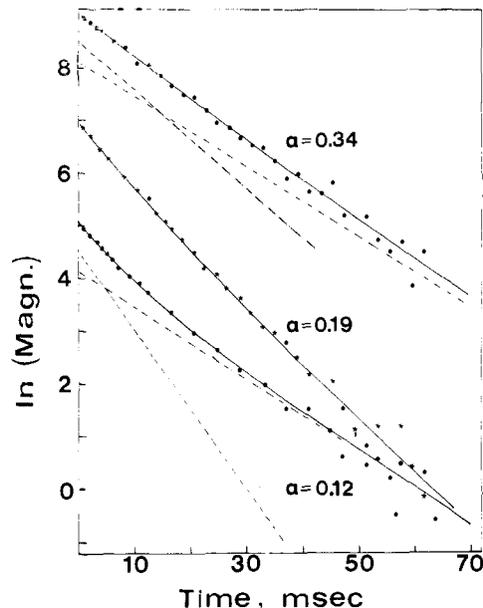


Figure 4. The natural logarithm of the ^{23}Na magnetization after a CPMG pulse sequence for three different α values. The solid lines are from the best fit of eq 2 to experimental data and the dashed lines indicate the contribution to total magnetization from the slow and fast relaxing components.

the slowly decaying part of the magnetization contributes to the measured T_2 . Thus, similarity in R_2 and $\pi\Delta\nu_{1/2}$ can be caused by both a very long and a very short correlation time.

In the α region where the two measures of the transverse relaxation rate are significantly different, a non-Lorentzian line shape is expected in the absorption spectra and, similarly, a nonexponential decay of the magnetization ought to be observable. Indeed, this is the case. In Figure 3, absorption spectra for $\alpha = 0.94$ and 0.06 are shown, which have very similar line widths at half height, but very different line shapes. Below each spectrum, a theoretical curve is drawn. For the high α , a Lorentzian curve with $T_2 = 1/\pi\Delta\nu_{1/2}$ is plotted, but for the other case a line composed of two Lorentzians is drawn. Obviously, the sum of two Lorentzians, weighted in accordance with theory, is a much better approximation of the observed line shape at low α than is a simple Lorentzian curve. Therefore, the two relaxation rates were evaluated from the absorption spectra in the α region 0–0.5. The results of the evaluation, carried out by simple visual inspection of the fit between experimental and theoretical spectra, are summarized in Table I, where the calculated τ_c values are also included. No more sophisticated fitting procedure was used in view of the inaccuracies caused by experimental errors in the line shape. For experimental reasons such as, e.g., a slight spin sideband intensity and/or a non-Lorentzian magnetic field inhomogeneity, the fast component is expected to be slightly exaggerated, and an error that increases with decreasing line width is expected. By fitting the transverse magnetization obtained with the CPMG technique to the weighted sum of two exponentials according to eq 2, the two relaxation rate constants can also be obtained. The deviation from simple exponential decay is not as easily detected by the eye in a plot of magnetization vs. delay time as when the logarithm of magnetization is plotted. In the latter case, nonexponential decay is seen as a deviation from linearity.

The natural logarithm of the observed magnetization for $\alpha = 0.34$, 0.19, and 0.12 is plotted as a function of time in Figure 4. The solid lines drawn are from the best fit to a biexponential model. The magnetization data for $\alpha = 0.34$ are rather closely

Table I. $^{23}\text{Na}^+$ Relaxation Rates and Correlation Times Evaluated from the Shape of the Absorption Spectra (at 26.46 MHz), $R_F = 19.5 \text{ s}^{-1}$

α	b_1, s^{-1}	b_2, s^{-1}	τ_c, ns
0.582	40	34	2.3
0.469	43	38	2.0
0.411	63	52	2.5
0.352	83	63	3.1
0.293	167	69	8.0
0.235	250	74	10.5
0.176	232	65	11.5
0.118	213	59	12
0.059	180	42	14

Table II. Rate Constants, b_1 and b_2 , and Correlation Times, τ_c , Obtained from the Transverse Magnetization in Carr-Purcell-Meiboom-Gill Pulse Experiments at 23.81 MHz, $R_F = 16.7 \text{ s}^{-1}$

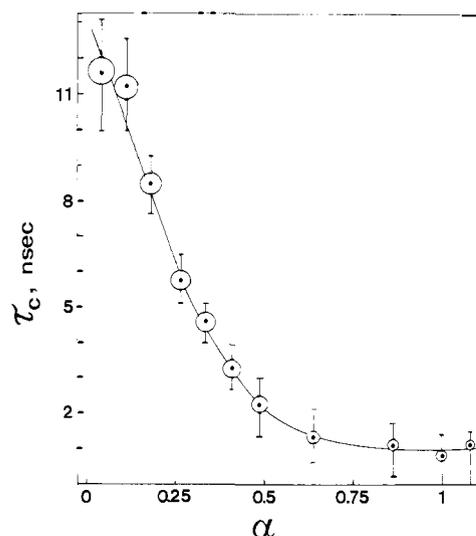
α	b_1, s^{-1}	b_2, s^{-1}	τ_c, ns
0.41	64	51.5	3
0.34	94	67.5	3.8
0.26	118	92	3.3
0.19	147	94.5	4.6
0.12	142.5	65.0	8.2
0.04	61.5	30.4	10

(but not completely) approximated by a single exponential, whereas for the lower degrees of neutralization, nonexponential relaxation is evident as shown by the curved plot in Figure 4. (The dashed lines show the logarithmic contributions to the magnetization from the fast and slow components, respectively, as resulting from the fit of the magnetization data. For $\alpha = 0.34$ the fast and slow relaxation rates are nearly the same, resulting in an approximately linear curve of $\ln(\text{total magn})$ vs. time. For the case $\alpha = 0.12$ the two slopes differ much more and the logarithm of the weighted sum is clearly nonlinear.) Nonlinear least-squares fits for α ranging from 0.04 to 0.41 gave the results reported in Table II. A comparison of the rate constant data in Tables I and II shows that the slow components (which are easily obtained with both methods) are very similar for comparable α . The fast component, b_1 , on the other hand, differs in the two cases. We have, so far, no really good explanation for this. It is possible that the fast relaxing component becomes slightly suppressed for some reason.

Thus we have evaluated the relaxation rates which can be used to obtain τ_c , following the three routes that are indicated in the Theory section. But τ_c can be accurately calculated only if $p_F R_F$ is known. R_F for $^{23}\text{Na}^+$ can, as has been shown previously, be considered practically unaffected⁷ by the presence of polyion and is therefore assigned the same value as observed in, e.g., an aqueous solution of NaCl of corresponding concentration. Thus, in the cases where longitudinal and transverse relaxation are encountered, 16.7 s^{-1} is used for R_F , and for calculations on relaxation rates obtained from absorption spectra 19.5 s^{-1} is used for the relaxation rate for the free ions. (The higher value in the latter case is due to the magnetic field inhomogeneity contribution to line widths.) The possible variation in R_F cannot appreciably affect the τ_c and $p_B \chi^2$ values deduced below. To see the effect of p_F on the calculated τ_c , it is illustrative to make calculations with extreme choices of p_F . Such extremes are first, as an upper limit, that all counterions are free ($p_F \rightarrow 1$) for all α , and second, as a lower limit, that all carboxylate sites are occupied with sodium. Here the fraction of free ions is given by the formula

$$p_F = 1 - p_B = 1 - \alpha C_p / C_{\text{Na}}$$

where C_p is the total concentration of monomeric units in PMA and C_{Na} is the total sodium concentration. Even if these limits

**Figure 5.** Correlation time, τ_c (ns), for the bound sodium ions in 0.47 *m* PMA as a function of α . τ_c is obtained from R_1 and R_2 of Figure 2 as described in the text, with $R_F = 16.7 \text{ s}^{-1}$.

(and especially the upper limit) are rather unreasonable, they do not produce any dramatic effects on the correlation times calculated. This is clear from the τ_c data calculated from eq 11 which are presented in Figure 5. The size of the circles in the figure indicates the τ_c limits due to the extreme p_F 's chosen. (The upper limit corresponds to the choice $p_F \rightarrow 1$, and the lower to the lower p_F extreme.) The estimated error due to the experimental uncertainty (indicated by the vertical bars) has a greater influence on the calculated correlation time for all α . But none of these uncertainties alters the main feature of Figure 5, i.e., the correlation time obtained with the aid of eq 11 varies appreciably with the degree of neutralization.

To have a more realistic function for the variation of p_F with α , some further considerations are needed. As was mentioned in the discussion of the PAA data, the concept of counterion condensation is frequently applied in discussions of counterion-polyion interactions. For PMA, as well as for PAA, "condensation" of counterions is assumed to start at an α of about 0.3.¹⁹ The idea behind the counterion condensation approach is that over a certain charge density ρ_c (the "critical" charge density) on the polyion, counterions are associated with the polyion in order to keep the "effective" density roughly equal to ρ_c . One easily finds that in a two-site model, p_F is given by

$$p_F = 1 \text{ when } \alpha < 0.3 \text{ and} \\ p_F = 1 - (\alpha - 0.3)C_p / C_{\text{Na}} \text{ for } 0.3 < \alpha \leq 1$$

The counterion condensation model will, however, not suffice to explain either the observation of maximal relaxation rates around $\alpha = 0.2$ or the observation of a very strong binding at high α . A strong binding at fully neutralized PMA is the most obvious interpretation of the data in Figures 2 and 3 of ref 7. Studies of the variation of the binding constant with α are in progress in our laboratory and we are presently exploring different approaches of ionic interactions in polyelectrolyte systems.

Therefore, in addition to the ion condensation also another function for counterion binding must be of importance. Quite arbitrarily, we choose the following function for the fraction of free counterions:

$$p_F = 1 - 0.45\alpha C_p / C_{\text{Na}} \quad \alpha \leq 0.3$$

and

$$p_F = 1 - (0.95\alpha - 0.15)C_p / C_{\text{Na}} \quad 0.3 < \alpha \leq 1 \quad (12)$$

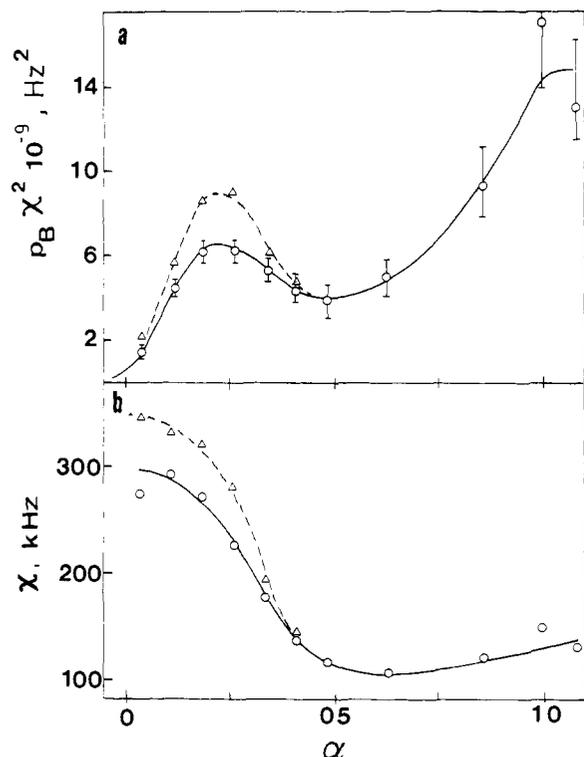


Figure 6. The quadrupole coupling constant, χ , and $p_B\chi^2$ for the bound sodium ions as a function of α for a 0.47 *m* aqueous PMA solution with 0.48 *m* sodium ion concentration. (a) $p_B\chi^2$ as obtained from relaxation rates in Figure 2 and τ_c from Figure 5, as a function of α . The error limits indicate the uncertainty in $p_B\chi^2$ due to uncertainty in p_F . Data obtained from the values in Table II are included (Δ). (b) Quadrupole coupling constants, χ (kHz), calculated from the data in Figure 6a and with p_F according to eq 12. In both (a) and (b), 16.7 s^{-1} is used for the relaxation rate of the free ions.

This corresponds to an average of counterion condensation and a strong association of ions which is linear in α (i.e., $p_B = 0.9\alpha C_p/C_{Na}$). This binding equation is used for the rest of this article, not because of any special significance of the function, but due to the fact that it does not produce any large errors in the deduced quantities for any neutralization degree.

The τ_c values given by the dots in Figure 5 are calculated on the basis of this p_F function chosen. (Direct information on the counterion binding may be obtained from studies of the effect on the NMR parameters of systematic variations of the ratio between counterion and polyion concentrations. Such studies are in progress.)

With the aid of eq 10 and with p_F given by eq 12, τ_c was calculated from the transverse relaxation rates in Tables I and II. The values obtained are included in the tables.

A comparison of correlation times from $\Delta(T_2/T_1)$ and from line shapes shows that the latter increase more rapidly at the lowest α values, while similar values are obtained for intermediate degrees of neutralization. Also for the correlation times from the transverse decay good agreement is obtained with the data of Figure 5 for the higher α values encountered, whereas for low α values lower τ_c values were obtained than with the $\Delta(T_2/T_1)$ evaluation procedure. The difference in τ_c from different methods, at low α values, is caused by the inaccuracy of the b_1 values in Tables I and II, respectively. Our conclusion is that the correlation times presented in Figure 5 are the most accurate owing to the fact that they are in a range where the approximative expression (eq 11) is expected to be valid and that some kind of systematic error in R_2 produces a lesser effect on the τ_c calculated from $\Delta(T_2/T_1)$ than from $\Delta(R_2)$. In any case, the overall picture provided is the same for all three cases: τ_c is rapidly decreasing with increasing α until about half-neutralization of PMA is reached.

As has already been pointed out in the theoretical section, the part of the relaxation expression due directly to ionic interactions, $p_B\chi^2$, can be deduced when τ_c is known. Values of this quantity, calculated with τ_c from either $\Delta(T_2/T_1)$ or the transverse decay, are given as a function of α in Figure 6a.

It is interesting to note that a variation following simply the assumed function for p_B is not observed. Again a maximum around $\alpha = 0.2$ emerges. The vertical bars on the curve indicate the limits of variation of $p_B\chi^2$ due to the extreme choices of p_F already used in the τ_c evaluation. Thus, so far the choice of function for the fraction of bound ions has not introduced any uncertainty that can critically affect the derived quantities. However, if we now want to separate the product $p_B\chi^2$ and quantify both p_B and the quadrupole coupling constant separately, caution has to be taken. Thus, the only safe way to obtain unambiguous values of χ is to perform a separate determination of p_B . But, within acceptable accuracy, a separation can be made.

To start with, we assume that the quadrupole coupling constant is the same for all degrees of neutralization. This gives a variation in p_B that deviates greatly from the assumed variation in p_B . Most important is that with a constant and reasonable value of χ we obtain the result that the amount of bound sodium exceeds the amount of $-\text{COO}^-$ present at α around 0.2. This is an extremely improbable situation. Therefore, it is concluded that a variation in p_B only cannot explain the maximum in $p_B\chi^2$ observed around $\alpha = 0.2$. Instead, by assuming that the p_B values obtained from eq 12 are reasonably close to reality, values of the quadrupole coupling constant were calculated. As presented in Figure 6b, the variation of χ resembles the change of τ_c with α . Noteworthy also is that the values obtained with the different τ_c 's are similar and do not at all change the major features of the variation. Of course, for this calculation rather limited changes in the choice of p_B can at high α values cause alterations in the χ curve. But, even in the limit of maximum binding (i.e., $p_B = \alpha C_p/C_{Na}$), an increase in χ must still be inferred for low α .

A change in the quadrupole coupling constant is in fact also expected from the chemical shift data presented in Figure 4 of ref 7. The anomalous α variation of the chemical shift indicates a change in the environment of the bound ions. Since χ and the chemical shielding should have some qualitative relation, both monitoring the interactions of the bound counterions, a change in χ is not unexpected.

Briefly summarized, the $^{23}\text{Na}^+$ relaxation data in PMA solutions presented show that in the region above $\alpha = 0.5$ the variation in relaxation is mainly due to a change in the fraction of bound counterions, while in the low α region changes in both the correlation time and the quadrupole coupling constant also are involved.

To relate the variation in the correlation time for the bound ions with a conformational change in the polymer is not entirely trivial. However, if the reorientation time of the polyelectrolyte dominates the correlation time, a variation in τ_c opposite to that observed would be expected. This is based on the generally assumed and accepted⁴⁻⁶ conformational change in PMA, which is from a (randomly) coiled to a more extended form with an increasing α . Therefore a direct relation between the polyion reorientation and the NMR correlation time is rejected.

Instead we propose that an internal motion (e.g., a segmental motion) within the polymer chain or the rate of counterion exchange between the bound and free states determines the correlation time, at least at high degrees of neutralization. Possibly both motions can make appreciable contributions to τ_c . At lower α these motions can be so seriously hindered that the rotational motion of the (coiled) PMA can give a significant contribution to τ_c . Without further experiments, none of

Table III. Longitudinal and Transverse Relaxation Rates, Correlation Times, and Quadrupole Coupling Constants for Different Degrees of Neutralization in 0.314 *m* Aqueous PMA with $C_{\text{Na}} = 0.25$ *m*, $R_{\text{F}} = 16.5$ s^{-1}

α	p_{F}^a	R_1, s^{-1}	R_2, s^{-1}	$\Delta(T_2/T_1)$	τ_c, ns	$p_{\text{B}}\chi^2 \times 10^{-10}$	χ, kHz
0.8	0.24	45.0	55.5	0.8	2.5	0.60	89
0.6	0.48	33.1	37.6	0.85	2.0	0.414	88.6
0.3	0.83	45.1	64.2	0.62	4.2	0.412	156
0.2	0.89	42.7	81.8	0.43	6.9	0.424	194
0.1	0.94	28.5	60.24	0.29	10.5	0.232	203

^a The values used for the fraction of free counterions are obtained from eq 12.

these motions can be excluded as unimportant, but some alternatives are tentatively discussed below.

The concentration dependence of the relaxation rate maximum around $\alpha = 0.2$ indicates that inter-PMA interactions play an increasingly important role with increasing PMA concentration. The most obvious implication of this is that an aggregation of PMA occurs. This may indicate that the contribution to τ_c from PMA reorientation is of little importance even at low degrees of neutralization (since rotation of complexes of (coiled) PMA is expected to be comparatively slow). If the relaxation maximum was simply a concentration effect a similar behavior would be expected for PAA. But, as shown in Figure 1, no change in τ_c justifying an assumption of inter-chain interactions is observed even at a 0.65 *m* concentration of PAA. A pronounced difference between PAA and PMA persists also at much lower polyion concentrations (e.g., less than 0.1 *m*). At low concentrations an aggregation of PMA is probably of minor importance. Therefore, in addition to aggregation, even an intramolecular conformational change must be of importance in PMA. The difference between the two polyelectrolytes can possibly be derived directly from the difference in molecular structure. The exchange of the methyl group in PMA for a hydrogen in PAA can tentatively be assumed to make the PAA chain so much more hydrophilic than PMA that PAA preferentially exists in an extended form also at very low charge densities. Furthermore, the difference in size of the methyl group and the hydrogen would be expected to result in a slower internal motion in PMA than in PAA.

Our preliminary interpretation of the maximum in the relaxation rate and the altered sign of the chemical shift⁷ was that specific complexes of $\text{Na}_{\text{aq}}^+ - \text{COO}^- - \text{COOH}$ should be of importance. If such complexes are formed within the polyion chain, then the segmental motion in PMA is expected to be reduced. For both inter- and intramolecular PMA complexes, a decrease in sodium ion exchange rate (or more accurately, an increase in the lifetime for bound ions) and a modified mode of sodium ion binding would also be expected.

If the proposal of interpolyion complexes is well founded, it would also be expected that the changes in both τ_c and χ should decrease with decreasing concentration of PMA since the occurrence of complexes between different PMA molecules

is much less probable at low concentrations. As a test of the hypothesis, relaxation rates, R_1 and R_2 , were measured for a 0.31 *m* PMA solution with a sodium ion concentration of 0.25 *m*. The relaxation rates as well as calculated values of τ_c , $p_{\text{B}}\chi^2$, and χ (with p_{B} from eq 12) are given in Table III.

Compared to the 0.47 *m* PMA solution a slight reduction in the correlation time can be inferred at low α . The reduction of the quadrupole coupling constant is significant over the full α range but is especially pronounced at the lower degrees of neutralization. Consequently, macromolecule-macromolecule interactions are significant at high polyion concentrations.

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