

qualitatively some subtle effects as the increase of P and Φ beyond the sphere limits. We can also perform a useful comparison of the transition curves that can be expected for different types of chains or properties. However, we cannot give a good quantitative description of the change of the properties with temperature in the form of scale laws or obtain the asymptotic values corresponding to the globular state. Of course, these type of results were not obtained in previous simulations for dimensions of linear chains with similar two-parameter intramolecular models.^{21,22} In summary, we conclude that simple models can describe tendencies but not detailed dependencies in the $T < \Theta$ region. Given this situation, future simulation work should be directed not only to improving the calculation efficiency through more efficient algorithms but also to studying alternative models applicable to both the globular and the expanded coil states with similar adequacy.

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Water Dynamics in Polyelectrolyte Solutions from Deuterium and Oxygen-17 Nuclear Magnetic Relaxation

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ABSTRACT: Longitudinal relaxation rates of D and ^{17}O were obtained in a concentration series of poly(acrylic acid) and poly(styrenesulfonic acid) solutions with various counterions. The effects of the degree of neutralization and excess simple electrolyte on the water dynamics have been investigated. From these data conclusions are reached about the range of the polyion-solvent dynamical perturbation. The dynamical behavior of water molecules is changed significantly as shown by the correlation times. The symmetry of the motion is discussed by comparison of D and ^{17}O relaxation.

I. Introduction

A multinuclear NMR investigation of water dynamics in low molecular weight electrolyte solutions was reported recently.¹ Mulder et al. reported a study of the anisotropic behavior of the solvent in poly(methacrylic acid) (PMA) solutions.² In the present contribution, results of D and ^{17}O NMR in poly(acrylic acid) (PAA) and poly(styrenesulfonic acid) (PSS) solutions are reported. In the interpretation of the nuclear relaxation of counterions in solutions of charged macromolecules the influence of the perturbed solvent dynamics is unknown. Apart from the intrinsic interest of the solvent behavior this is an additional motivation for the present investigation.

Although many proton relaxation studies of water dynamics in various solutions have been reported, an unambiguous interpretation is difficult. The proton longitudinal relaxation is governed by H-H dipolar interactions. The intra- and intermolecular contributions to the proton relaxation are of the same order of magnitude. As a consequence, a determination of the intramolecular contribution is very sensitive to the correctness of the estimation of the intermolecular part. However, both the D and ^{17}O

nuclei relax by the quadrupolar interaction mechanism, which is dynamically an intramolecularly determined process, although the coupling constants may depend on the intermolecular interactions. Hence, the NMR spin-lattice relaxation time values are sensitive to the single molecular reorientational motion. Especially, because the principal directions of the interaction tensors of ^{17}O and D do not coincide, the symmetry of the motion may be investigated.³

Due to the possibly high linear charge density on polyions, in polyelectrolyte solutions the oppositely charged counterions may be strongly attracted by the charged chain. A useful description of the resulting distribution of counterions around the polyion is the Oosawa-Manning model.^{4,5} The linear charge density on the polyion is described by the charge density parameter, ξ , ξ being the ratio of the electrostatic energy between neighboring charges on the chain to the thermal energy

$$\xi = e^2 / 4\pi\epsilon_0\epsilon A kT \quad (1)$$

Here, A denotes the distance between neighboring charged beads on the chain and the other symbols have their usual

meaning. According to the Oosawa-Manning model, for $\xi > 1$ a certain fraction of counterions is clustered around the polyion, thereby reducing the charge density parameter to unity. The other small ions will be influenced by a much smaller potential, because of the lower effective charge on the chain.

In low molecular weight electrolyte solutions, the water nuclei relaxation rates are usually decomposed into the contributions of the ionic species present in solution.⁶ Due to the accumulation of small ions around the charged chain, in polyelectrolyte solutions a breakdown of the experimental relaxation rates into separate contributions of polyions and counterions is not feasible. Especially, from the work reported here, the importance of the counterion-polyion interaction is indicated. Hence, in macromolecular systems the relaxation behavior of water nuclei is usually described by a two-phase model.⁷ The observed relaxation rate is decomposed into two contributions. One originates from water molecules dynamically perturbed by the polyion and its condensed counterions. The other contribution originates from the remaining part, in which the uncondensed counterions are solvated. These two phases are distinguished by the labels p (perturbed) and u (unperturbed), respectively.

An important feature is the range of the solvent perturbation caused by the macromolecular surface. Many studies show this range to be confined to one or two molecular layers. Among them are NMR and neutron scattering experiments on the surface effect of silica,⁸ clay,⁹ and phospholipids.¹⁰ Recent neutron and X-ray scattering experiments show the hydration shell of PMA to consist of about 18 molecules per monomer only, with an increase in density on the order of 8%.¹¹ A recent MD simulation study shows an increase in local water density by a factor of 2, induced by a mica surface with two associated counterions.¹² The range of this increase in local water density was found to be confined to a molecular layer of two from the surface to the bulk.

In section II the D and ¹⁷O relaxation equations are presented, which relate the macroscopic rates to the single molecular reorientational motion. After section III, the results are presented in section IV. Comparison is made to low molecular weight electrolyte solutions. In section IV.A the two-phase model is presented, extended with some modifications to take into account the effect of counterions on the water dynamics. The range of the polyion-solvent interaction and the unperturbed water dynamical properties are evaluated in section IV.B. To this end, the influence of the type of counterion, the side group, the degree of neutralization, and excess simple salt on the observed water relaxation behavior is considered. Perturbed water reorientational correlation times and reorientational symmetry are discussed in section IV.C. Finally, in section V the main conclusions are summarized.

II. Theory

Early work on PAA and fully neutralized PMA solutions showed the water reorientational motion to occur on the picosecond time scale.^{2,13} As a consequence the extreme narrowing condition is fulfilled. The D and ¹⁷O longitudinal relaxation rates are determined intramolecularly by the quadrupolar interaction

$$R_D = \frac{3}{8}(2\pi\chi_D)^2(1 + \eta_D^2/3)\tau_D \quad (2)$$

for the D nucleus and for ¹⁷O

$$R_O = \frac{3}{125}(2\pi\chi_O)^2(1 + \eta_O^2/3)\tau_O \quad (3)$$

in which χ_D and χ_O denote the D and ¹⁷O quadrupole

coupling constant, respectively. The asymmetry parameters of the D and ¹⁷O electric field gradients are denoted by η_D and η_O , respectively.

The correlation times τ_D and τ_O are the zero frequency Fourier components of the correlation functions of the interaction tensors. These correlation times contain all the dynamical features that can be obtained from NMR, irrespective of the details of the motion. Because the relaxation processes are intramolecularly determined, these correlation times refer to the reorientational dynamics only. Because the principal directions of the D and ¹⁷O interaction tensors do not coincide, a possible anisotropy in the solvent reorientational motion may be investigated.

The effective correlation times of perturbed water will be analyzed by a reorientational diffusion process having axial symmetry. For a study of the relative relaxation behavior of D and ¹⁷O as a function of the diffusion tensor properties, ref 3 may be consulted. The diffusion tensor is characterized by two components $D_{||}$ and D_{\perp} and by the orientation of the principal axis system of this tensor with respect to the molecular frame. Under extreme narrowing conditions the effective correlation times are given by¹⁴

$$\tau_x = \frac{1}{\sum_{\vec{k}} |V_k^{(2)}|^2} \sum_{\vec{k}} V_k^{(2)} V_l^{(2)*} D_{km}^{(2)}(\Omega_x) D_{lm}^{(2)*}(\Omega_x) \tau_{|m|} \quad (4)$$

with

$$\tau_m^{-1} = 6D_{\perp} + m^2(D_{||} - D_{\perp}) \quad (5)$$

The Wigner matrix $D^{(2)}$ describes the transformation of the principal axis system of the interaction tensor to the principal axis system of the diffusion tensor, characterized by the orientation Ω_x . The lattice part of the coupling Hamiltonian, i.e., the interaction tensor, is described by the irreducible elements $V_k^{(2)}$. In the principal axis system of the quadrupolar interaction, one has $V_0^{(2)} = \text{eq } (3/2)^{1/2}$, $V_{\pm 1}^{(2)} = 0$, and $V_{\pm 2}^{(2)} = -\text{eq } \eta/2$. The subscript x can be O or D when the relaxation path is respectively oxygen-17 or deuterium quadrupolar interaction.

III. Experimental Section

A. Chemicals and Solutions. All solutions were prepared by weight. Concentrations are given as the number of moles of monomeric units per 55.5 mol of water, i.e., the monomolality (\bar{m}). Oxygen isotopically enriched water was obtained from Monsanto Research Corp., containing 9.9% ¹⁶O, 51.1% ¹⁷O, and 39.0% ¹⁸O. D₂O was obtained from Ventron GmbH. Distilled water was deionized and filtered by a Milli-Q water purification system (Millipore Corp). All manipulations with isotopically enriched water were performed at 5 °C to minimize exchange with atmospheric humidity.

NMR tubes (Wilmad 10 mm) were heated in a NaHCO₃ solution, heated in an EDTA solution, and then stored for at least 1 week filled with deionized and filtered water.

PAA, degree of polymerization (DP) = 2700 and 4200, was synthesized and fractionated as described before.¹⁵ DP was determined by viscosity measurements, in the presence of 0.01 N HCl, using Mark-Houwink relations.¹⁵ NaPSS, DP = 240 (Pressure Chemicals), was brought into the acid form by an ion-exchange resin. Polyacid concentrations were determined by potentiometric titration. Potassium acetate (KAc) originated from Baker.

PAA, DP = 2700, was fully neutralized with LiOH, NaOH, KOH, and RbOH to obtain the corresponding salts. PSS was fully neutralized with NaOH and KOH. KOH and NaOH were obtained from Merck. RbOH originated from ICN Pharmaceuticals. LiOH was gold label quality from Aldrich. To obtain the concentration series, samples of stock solutions, to which some D₂¹⁷O was added, were stepwise concentrated by means of evaporation in the tubes. NMR measurements were performed in between. The evaporation took place in a vacuum oven at room temperature

Table I
Isotope-Effect-Corrected Relaxation Rates and Isotopic
Composition of Fully Neutralized Samples^a

solute	c_p, \bar{m}	n	$p17$	$p18$	R_D^0, s^{-1}	R_O^0, s^{-1}
LiPAA	0.47	0.033	0.008	0.008	2.70	196
	1.45	0.033	0.008	0.008	4.43	333
	3.05	0.180	0.044	0.034	8.01	666
	3.86	0.086	0.021	0.017	10.9	937
	6.57	0.086	0.021	0.017	32.6	3470
NaPAA	7.25	0.278	0.062	0.153	46.6	5550
	0.66	0.033	0.008	0.022	2.66	202
	1.21	0.033	0.008	0.022	3.37	249
	1.73	0.150	0.036	0.040	4.06	308
	2.10	0.039	0.010	0.009	4.61	359
KPAA	4.05	0.159	0.039	0.030	9.80	785
	4.94	0.090	0.022	0.018	12.7	1060
	7.44	0.159	0.039	0.030	33.7	3310
	8.16	0.285	0.065	0.143	47.9	4830
	0.66	0.041	0.009	0.028	2.49	180
RbPAA	1.34	0.041	0.009	0.028	3.03	219
	1.65	0.043	0.011	0.010	3.18	238
	2.25	0.139	0.033	0.042	3.80	280
	4.23	0.122	0.030	0.023	6.01	461
	6.84	0.180	0.044	0.033	10.4	815
NaPSS	8.26	0.122	0.030	0.023	14.3	1240
	0.52	0.027	0.007	0.007	2.33	170
	1.15	0.187	0.046	0.035	2.80	207
	2.27	0.187	0.046	0.035	3.62	283
	2.64	0.176	0.043	0.033	4.05	310
KPSS	5.33	0.176	0.043	0.033	7.26	615
	0.46	0.036	0.009	0.008	2.20	163
	1.32	0.180	0.044	0.034	2.72	209
	1.53	0.018	0.005	0.005	2.88	224
	3.34	0.080	0.044	0.034	4.37	378
KAc	3.70	0.018	0.005	0.005	4.70	413
	0.46	0.041	0.010	0.009	2.19	157
	1.05	0.192	0.047	0.036	2.36	179
	1.82	0.047	0.012	0.010	2.65	205
	4.19	0.532	0.119	0.282	3.82	334

^a n , $p17$, and $p18$ denote the D, ¹⁷O, and ¹⁸O mole fraction, respectively.

in nitrogen atmosphere and at a pressure of 10–15 mmHg in the presence of P₂O₅.

Partially neutralized NaPAA, LiPAA, and CsPAA, DP = 4200, solutions were prepared. Solutions with excess simple salt were obtained by stepwise addition of LiCl and CsCl (Aldrich, gold label quality) to the partially neutralized LiPAA and CsPAA samples, respectively. Some H₂¹⁷O was added and NMR measurements were performed in between.

B. Determination of the Relaxation Rates. Concentration series were measured on a home-modified Bruker BKR spectrometer equipped with a 1.4-T Varian electromagnet. Partially neutralized NaPAA samples were measured on a home-built spectrometer equipped with a 2.1-T Bruker electromagnet. The temperature was maintained at 298 ± 0.2 K by a fluid thermostat by using Fluorinert grade FC-43 (3M Co.). The magnetic field was locked with an external lock probe, using the F resonance in trifluoroacetic acid doped with copper acetate. Partially neutralized CsPAA and LiPAA samples and solutions with excess simple salt were measured on a home-modified Bruker SXP spectrometer equipped with a 6.3-T superconducting magnet (Oxford Instruments). The temperature was maintained at 298 ± 0.5 K with a variable-temperature unit (Bruker B-VT 1000).

T_1 relaxation times were obtained at least in duplicate by the inversion recovery method with an estimated accuracy of 2%. FID's were accumulated, while the relative phase of the π and the $\pi/2$ pulses was alternated.¹⁶ The longitudinal relaxation was observed to be single exponential for all samples studied. A least-squares fitting procedure was used to obtain the relaxation rates. No field dependence of relaxation rates was observed.

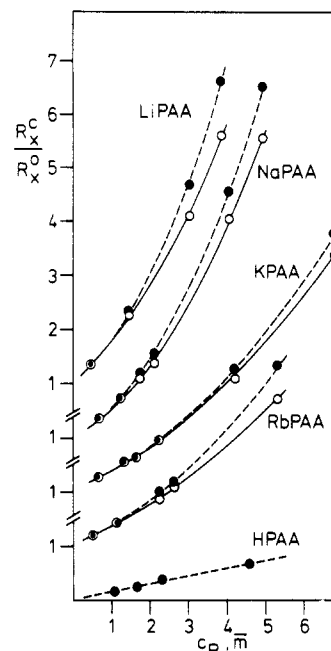


Figure 1. Isotope-effect-corrected longitudinal relaxation rates of fully neutralized solutions and HPA divided by the pure water values vs the concentration. For the different nuclei the following notations are used: ¹⁷O, filled symbols; D, open symbols. Curves are drawn to a quadratic polynomial fit. Dashed curves, ¹⁷O relaxation; solid curves, D relaxation.

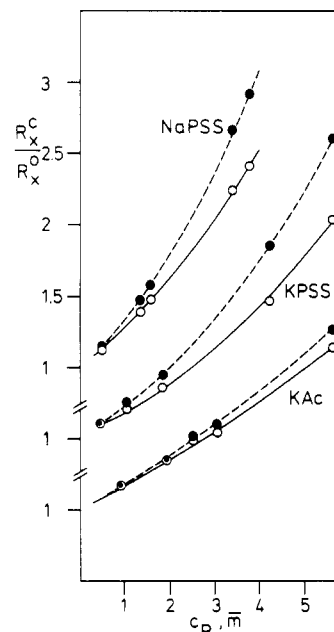


Figure 2. As in Figure 1, but for fully neutralized polystyrenesulfonic acid solutions and potassium acetate.

Isotope effects on the relaxation rates were corrected as described before.¹ Samples were enriched as little possible, leading to small corrections for isotope effects on the order of 1%.

IV. Results and Discussion

A. Concentration Dependence of the Relaxation Rates. D and ¹⁷O relaxation rates in fully neutralized PAA, PSS, and the low molecular weight KAc solutions are presented in Table I. The solutions are fully neutralized, because D site binding to polyelectrolyte acid groups enhances the spin-lattice relaxation.¹⁷ The ratio of the relaxation rates to the corresponding pure water values are displayed in Figures 1 and 2 as a function of the polyelectrolyte concentration c_p . At 298 K the pure water values are $R_D^0 = 1.944 \pm 0.004 s^{-1}$ and $R_O^0 = 141.6 \pm 0.5$

s⁻¹.¹⁸ The importance of the connectivity of the charged beads is indicated by the observed difference in relaxation rates between PAA and KAc solutions.

As discussed in the Introduction, the data will be interpreted by the two-phase model. The relaxation rate of water dynamically perturbed by the polyelectrolyte chain and its condensed counterions is denoted by R_x^p . For the remaining part, in which the uncondensed counterions are solvated, the relaxation rate is denoted by R_x^u . If the perturbed water phase consists of more classes of water, the relaxation rate R_x^p should be interpreted as an effective averaged quantity. Especially the contribution of the uncharged backbone will be discussed below. The experimental relaxation rate can now be decomposed into the contributions of the perturbed and unperturbed water phases¹⁹

$$R_x^c = fR_x^p + (1 - f)R_x^u \quad (6)$$

All relaxation rates are understood to be corrected for small isotope effects, this is indicated by the superscript *c* for R_x^c only.

Equation 6 is valid when the residence time of a water molecule within a phase is longer than the reorientational time scale and shorter than the macroscopic relaxation times. With this model, the intrinsic reorientational time scales turn out to be in the picosecond range. The latter condition is easily satisfied, because the shortest measured relaxation time is about 2×10^{-4} s. The residence times are unknown. However, due to the electrostatic origin of the polyion-solvent interaction, these times are expected to be longer than the intrinsic reorientational time scales.

In eq 6 *f* denotes the monomole fraction perturbed water. If a hydration number *n* is defined, the fraction *f* may be expressed in terms of the monomolality c_p of the solution

$$f = nc_p/55.5 \quad (7)$$

The hydration number *n* represents the range of the polyion-solvent interaction. The two-phase model becomes inappropriate when the fraction of hydration water approaches unity. This is certainly true for concentrations exceeding, say, 5 *m*. However, in this contribution, the two-phase model will be applied for the low concentration range to obtain the perturbed water relaxation rates induced by a diluted polyion.

According to eq 6 and 7, the two-phase model demands a linear dependence of the observed relaxation rates on the concentration c_p . In the range 0.1–0.6 *m* the linearity of the ¹⁷O transverse relaxation in PAA and fully neutralized PMA solutions was reported before.¹³ As displayed in Figures 1 and 2, in concentrated fully neutralized polyelectrolyte solutions curvature in the concentration dependence of the relaxation rates is observed. This implies that the hydration number *n* and/or the rates R_x^p and R_x^u depend on the concentration. The electrostatic origin of this effect is indicated by the observed linear concentration dependence of ¹⁷O rates in unneutralized PAA solutions (see Figure 1). The degree of self-dissociation in, e.g., a 1.09 *m* HPAA solution is about 3×10^{-3} , as determined by pH measurement. Unneutralized PAA is nearly uncharged. As will be discussed below, the water nuclei relaxation rates are to a large extent determined by the dynamical perturbation in close proximity to the chain. As an approximation, in the low concentration range the hydration number *n* is assumed to be constant. The observed curvature is assigned to the concentration dependence of the intrinsic relaxation rates R_x^p and R_x^u .

To describe the relaxation behavior of perturbed and unperturbed water a polynomial expansion in the poly-

electrolyte concentration will be applied. Within the unperturbed phase the solvated counterions will influence R_x^u in a manner similar to the situation in simple electrolyte solutions. In low molecular weight electrolyte solutions, the water nuclei relaxation is usually described by a polynomial expansion in the molality.⁶ Hence, the unperturbed water relaxation rate may be expressed as

$$R_x^u/R_x^0 = 1 + b_x^0 c_p + b_x^1 c_p^2 + \dots \quad (8)$$

in which b_x^0 and b_x^1 represent the influence of small ions on R_x^u . As will be shown below, these coefficients are comparable to the linear and quadratic terms of the polynomial expansion in simple salt solutions.

As will be discussed below, the accumulation of small ions around the polyion causes a considerable increase in water nuclei relaxation rates. According to the Oosawa-Manning model the fraction of condensed counterions does not depend on the polyelectrolyte concentration.^{4,5} However, in these concentrated solutions the inter-distance between different polyelectrolyte segments is short. Therefore, with increasing polyelectrolyte concentration, penetration of small ions into the perturbed region is likely to occur. A decreased dissociation of highly concentrated polysalts with increasing concentration is also indicated by apparent molal volume studies.²⁰ Accordingly, the perturbed water relaxation rate R_x^p depends on the concentration. Another effect is due to the interaction of the hydration layers of different polyelectrolyte segments. To describe the concentration dependence, again a polynomial expansion is applied

$$R_x^p/R_x^{p0} = 1 + d_x^0 c_p + d_x^1 c_p^2 + \dots \quad (9)$$

in which R_x^{p0} denotes the perturbed water relaxation rate induced by a diluted polyion with condensed counterions. Inserting eq 7–9 into eq 6 then yields the final expression of the experimental observed relaxation rate as a function of the polyelectrolyte concentration

$$R_x^c/R_x^0 = 1 + B_x c_p + C_x c_p^2 + \dots \quad (10)$$

with

$$B_x = \frac{n}{55.5} \left[\frac{R_x^{p0}}{R_x^0} - 1 \right] + b_x^0 \quad (11)$$

and

$$C_x = \frac{n}{55.5} \left[\frac{R_x^{p0}}{R_x^0} d_x^0 - b_x^0 \right] + b_x^1 \quad (12)$$

Fitted quadratic polynomials are displayed in Figures 1 and 2. In the range 0–6 *m* they describe the relaxation behavior well. For higher concentrations eq 10 has to be extended with terms of higher order. Coefficients B_x and C_x resulting from the fit of eq 10 to the data displayed in Figures 1 and 2 are presented in Table II.

In section IV.B the range of the polyion-solvent interaction and the unperturbed water dynamical properties are evaluated. For this purpose, the effects of the type of counterion, side group, degree of neutralization, and excess simple salt on the relaxation behavior are considered.

B. Effects of the Polyion-Counterion Interaction on the Water Dynamics. Influence of Type of Counterion and Side Group. As indicated by the fitted parameters presented in Table II, the water relaxation in polyelectrolyte solutions with various counterions is more enhanced compared to, e.g., that in the corresponding simple chloride solutions.¹ For comparison, the linear

Table II
Linear and Quadratic Coefficients of the Polynomial Expansion of R_1^0/R_1^0 in (Mono)molality

solute	B_D, \bar{m}^{-1}	B_O, \bar{m}^{-1}	C_D, \bar{m}^{-2}	C_O, \bar{m}^{-2}
HPAA		0.15 ± 0.01		
LiPAA	0.64 ± 0.09	0.57 ± 0.09	0.14 ± 0.03	0.23 ± 0.03
NaPAA	0.37 ± 0.03	0.34 ± 0.03	0.151 ± 0.007	0.195 ± 0.006
KPAA	0.31 ± 0.02	0.31 ± 0.01	0.047 ± 0.003	0.056 ± 0.002
RbPAA	0.31 ± 0.01	0.30 ± 0.01	0.038 ± 0.003	0.061 ± 0.003
KAc	0.168 ± 0.008	0.172 ± 0.007	0.006 ± 0.002	0.010 ± 0.002
NaPSS	0.264 ± 0.003	0.282 ± 0.007	0.032 ± 0.001	0.064 ± 0.002
KPSS	0.16 ± 0.02	0.19 ± 0.01	0.020 ± 0.005	0.033 ± 0.002
LiCl ^a	0.102 ± 0.008	0.072 ± 0.009		
NaCl ^a	0.05 ± 0.01	0.022 ± 0.008		
KCl ^a	-0.027 ± 0.003	-0.021 ± 0.001		
CsCl ^a	-0.041 ± 0.003	-0.030 ± 0.005		

^a Reference 1.

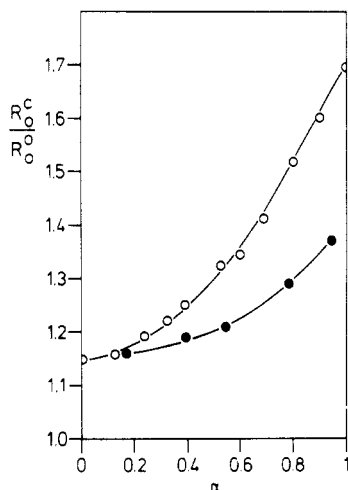


Figure 3. Relative ^{17}O longitudinal relaxation rates vs. the degree of neutralization α . For the different salts the following notations are used: NaPAA, open symbols; CsPAA, filled symbols. Concentrations: NaPAA, $c_p = 1.09 \bar{m}$; CsPAA, $c_p = 0.99 \bar{m}$. Curves are drawn as an aid to the eye.

coefficients B_x of LiCl, NaCl, KCl, and CsCl solutions are also presented in Table II. The effect of RbCl on the water dynamics is comparable to the effect of CsCl.⁶ With decreasing size of cation, the water nuclei relaxation rates increase; i.e., according to the sequence: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \sim \text{Rb}^+$. As displayed in Figure 3, in partly neutralized NaPAA and CsPAA solutions this effect is also observed. In PAA solutions the water relaxation is to a larger extent enhanced compared to that in PSS solutions with a common counterion. The water nuclei relaxation rates depend on the nature of the polyion as well as the counterion.

A recent neutron and X-ray scattering experiment on PMA solutions shows a monomolecular hydration layer between the charged backbone and the condensed counterions.¹¹ The density of this intermediate hydration water is about 8% higher with respect to the bulk value. Like the water nuclei relaxation rates, the apparent molal volumes of polyelectrolytes with various counterions show large differences.^{20,21} With decreasing size of counterion, the electrostriction effect increases. A possible explanation for the counterion specificity of the relaxation rates is the polyion-counterion interaction. Due to the higher electric field intensity on the surface, smaller counterions have a stronger interaction with the polyion. As a consequence of this interaction, smaller counterions accumulate closer to the charged backbone. Concurrently, this induces an increase in local water density in close proximity to the polyion. As a result, the water reorientational mobility is reduced to a larger extent. The reorientational mobility is directly related to the relaxation rates according to eq

Table III
 ^{17}O Relaxation Rates of Partially Neutralized NaPAA ($c_p = 1.09 \bar{m}$) and CsPAA ($c_p = 0.99 \bar{m}$)^a

α	NaPAA		α	CsPAA	
	R_O, s^{-1}			R_O, s^{-1}	
0.13	164		0.17	164	
0.24	169		0.39	169	
0.32	173		0.54	172	
0.34	177		0.78	183	
0.52	188		0.94	194	
0.60	190				
0.69	200				
0.80	215				
0.90	227				
1.00	240				

^a α denotes the degree of neutralization.

2 and 3. Hence, a reduction in reorientational mobility causes an increase in rates. The difference in water nuclei relaxation rates according to the nature of the polyion can be interpreted in similar terms.

The sulfonic side group of PSS is bulkier than the carboxylate group of PAA. For instance, this is indicated by the apparent molal volumes of PSS and PAA with a common counterion.²¹ With decreasing size of side group, the water nuclei relaxation rates increase. If, due to the bulkier side group of PSS, more water molecules per monomeric unit are dynamically perturbed, the opposite effect is expected. Therefore, a difference in hydration number is not a probable explanation. As in case of the counterion specificity of the relaxation, this effect can also be interpreted in terms of the distance of closest approach of a counterion to the backbone. Due to the bulkier side group of PSS, the counterions do not condense as close to the backbone as in case of PAA. Concurrently, the water reorientational mobility is reduced to a lesser degree, which results in a less enhanced relaxation.

Differences in rates are observed according to the nature of both the polyion and counterion. These effects are interpreted in terms of the polyion-counterion interaction. The distance of closest approach of a counterion to the backbone is an important feature. This indicates the solvent dynamical perturbation to be confined to one or two molecular layers from the surface to the bulk. The remaining solvent has dynamical properties which are probably similar to the properties of water in simple electrolyte solutions. To probe these points of view, the effects of degree of neutralization and excess simple salt on the water relaxation are investigated.

Influence of Degree of Neutralization. ^{17}O relaxation rates of partly neutralized NaPAA and CsPAA solutions ($c_p = 1.09$ and $0.99 \bar{m}$, respectively) are presented in Table III. They are displayed in Figure 3 as a function

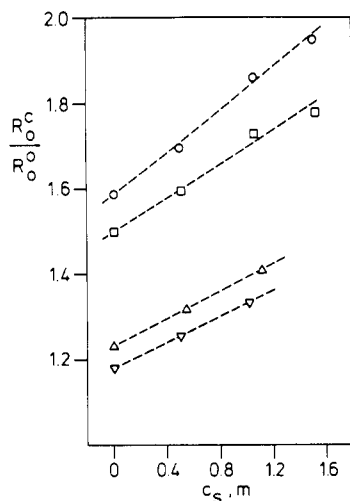


Figure 4. Relative ^{17}O longitudinal relaxation rates of partially neutralized LiPAA solutions ($c_p = 0.82\text{ m}$) vs the concentration excess of LiCl, c_s . For the different degrees of neutralization the following symbols are employed: (O) $\alpha = 0.97$; (□) $\alpha = 0.90$; (Δ) $\alpha = 0.42$; (▽) $\alpha = 0.26$. Curves are drawn as an aid to the eye.

of the degree of neutralization α . In a 1.09 m unneutralized PAA solution the ^{17}O relaxation is still 15% enhanced compared to the pure water value. The exchange-modulated scalar interaction contribution to the ^{17}O longitudinal relaxation is negligible.²² The effect of the nearly uncharged PAA chain on the water dynamics is not negligible. This is in agreement with results in solutions of polyethylene oxide, which is an uncharged polymer.²³ With increasing α the charge on the polyion increases. The ^{17}O relaxation is observed to increase with increasing degree of neutralization. This effect is more pronounced in NaPAA solutions compared to CsPAA solutions with a roughly equal monomolality. The counterion specificity of the relaxation enhancement, as observed in fully neutralized solutions, is present in the whole α -range.

As discussed in the Introduction, according to the Oosawa-Manning model, when the parameter ξ exceeds unity a certain fraction of counterions is clustered around the polyion. According to this model this fraction equals $1 - \xi^{-1}$, but in these concentrated solutions this value is probably somewhat higher. At 298 K, in PAA solutions, $\xi \geq 1$ when $\alpha \geq 0.35$. As displayed in Figure 3, the accumulation of small ions around the chain is accompanied by a considerable increase in solvent nuclear relaxation rate. This result is in accordance with the conclusion reached above. The solvent dynamical perturbation was indicated to be confined to the vicinity of the polyion. On charging the polyion, the condensing counterions penetrate into the perturbed phase. Thereby, the water reorientational mobility in close proximity to the chain is reduced, which results in an enhanced ^{17}O relaxation.

To allow an evaluation of the unperturbed water dynamical properties and the effect of polyelectrolyte conformation, the influence of added excess simple salt on the relaxation is investigated.

Influence of Excess Simple Salt. The ^{17}O relaxations in partly neutralized LiPAA and CsPAA solutions with excess LiCl and CsCl, respectively, are displayed in Figures 4 and 5. The relative influence of excess salt on the relaxation does not depend on the linear charge density on the polyion. Excess LiCl enhances the relaxation, while in case of CsPAA solutions the structure-breaking effect of CsCl is observed. These relative effects are in qualitative accordance with the water relaxation behavior in the corresponding chloride solutions without the presence of polyions.¹

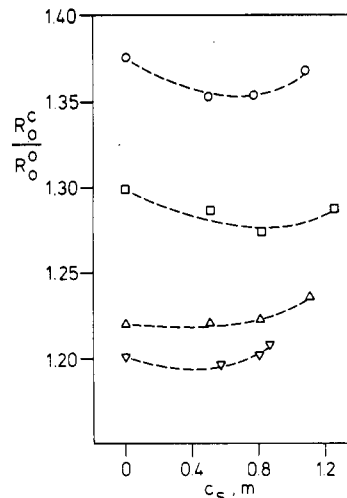


Figure 5. As in Figure 4, but for CsPAA solutions ($c_p = 0.99\text{ m}$) with excess CsCl. For the different degrees of neutralization the following symbols are employed: (O) $\alpha = 0.94$; (□) $\alpha = 0.78$; (Δ) $\alpha = 0.54$; (▽) $\alpha = 0.39$.

According to the additivity rule,⁵ addition of simple salt does not increase the number of small ions in close vicinity of the polyion. Hence, excess simple salt is solvated within the unperturbed phase. According to eq 6, i.e., the two-phase model, the influence of added salt on R_0^u is additive to the observed rate R_0^c . As shown in Figures 4 and 5 the relaxation rates increase linearly with the LiCl concentration whereas the influence of CsCl is nearly negligible. Qualitatively this is in concordance with the influence of these salts in the absence of polyelectrolytes. Quantitatively, however, the rate of increase of the ^{17}O relaxation due to excess LiCl is roughly twice as large as its value in simple chloride solutions.¹ In this case a simple additivity rule does not seem to be valid.

The influence of polyelectrolyte conformation on the water dynamics is of minor importance, as shown by the results in solutions with excess simple salt. Due to excess simple salt the electrostatic intramolecular repulsion decreases. As a consequence, the polyelectrolyte backbone becomes more flexible and the viscosity of the solution is reduced. However, as shown for instance by CsPAA solutions with excess CsCl, this decrease in polyion stiffness does not effect the water relaxation.

The effects of the type of counterion, the side group, the degree of neutralization, and excess simple salt show the two-phase model to be an adequate approximation. The solvent dynamical perturbation is confined to the close vicinity of the polyion, where the condensed counterions have a remarkable influence on the dynamics. Due to this effect, a breakdown of relaxation rates into contributions of polyions and counterions is not feasible. The uncondensed counterions influence the unperturbed water relaxation behavior in a manner similar to the situation in the corresponding chloride solutions. The effect of polyelectrolyte conformation is of minor importance. Now, from the linear coefficients B_x , perturbed water reorientational correlation times are calculated. The symmetry of the motion is investigated by comparison of D and ^{17}O relaxation, both for the low concentration limit and for finite concentrations.

C. Perturbed Water Reorientational Correlation Times and Motional Symmetry. Low Concentration Limit. The ratio R_x^{p0}/R_x^0 represents the ratio of the perturbed water relaxation rate induced by an isolated polyion to the pure water value. However, according to eq 11, to calculate this quantity from the linear coefficients B_x , values of the hydration number n and the coefficient

b_x^0 have to be estimated. The exact value of the hydration number is unknown, although the solvent perturbation was indicated to be confined to the vicinity of the polyion. As an upper limit, a value of 15 is used, i.e., the number of water molecules which are involved to form a monomolecular hydration layer per monomer. As a lower limit, the correlation times are calculated with $n = 6$. This is approximately the primary hydration number as derived from volumetric properties of PAA salt systems.²⁰

The coefficient b_x^0 represents the influence of uncondensed counterions on R_x^u . As was discussed in section IV.B, this influence is comparable to the effect of the corresponding cations in simple chloride solutions. The effect of the Cl^- ion on the water dynamics is negligible.¹ Hence, the coefficient b_x^0 can be related to the B_x coefficient of the chloride solution containing the same counterion. To this end, the fraction of counterions which are solvated within the unperturbed region has to be estimated. As an approximation, this fraction is assumed to be the same as the fraction of uncondensed counterions according to the Oosawa-Manning model.^{4,5} According to this model, the fraction of uncondensed counterions equals ξ^{-1} . At 298 K, in fully neutralized PAA and PSS solutions $\xi^{-1} = 0.35$. Accordingly, the coefficient b_x^0 may be expressed as

$$b_x^0 = 0.35B_x(\text{MCl}) \quad (13)$$

in which $B_x(\text{MCl})$ represents the initial slope of the relaxation rate in the corresponding chloride solution.

The ratio R_x^{p0}/R_x^0 reflects the relative change in coupling constants and correlation times, according to

$$\frac{R_x^{p0}}{R_x^0} = \left[\frac{\chi_x^{p0}}{\chi_x^0} \right]^2 \frac{(1 + \eta_x^{p0/2}/3)}{(1 + \eta_x^{0/2}/3)} \frac{\tau_x^{p0}}{\tau_x^0} \quad (14)$$

The coupling constants and the correlation times are known reasonably well in pure water.^{24,25} In pure water, the reorientational motion was demonstrated to be isotropic, within present experimental accuracy. Therefore, the pure water reorientational motion can be represented by one correlation time

$$\tau_x^0 = 1.95 \pm 0.08 \text{ ps} \quad (15)$$

for both D and ^{17}O relaxation. This value was obtained from ^{17}O enhanced H relaxation in ^{17}O enriched water. The small D-isotope effect on the correlation time is assumed to be equal for both perturbed and pure water.¹⁸

Previous work on electrolyte solutions shows the change in coupling constants induced by monovalent ions to be small.^{1,26} The ^{17}O coupling constant is nearly proportional to the D coupling constant, as was indicated in 4 *m* LiCl, NaCl, and KF. Hence, a study of water dynamics by comparing D and ^{17}O relaxation is not particularly sensitive to this effect. Also in view of the uncertainty in hydration number, the ratio $\chi_x^{p0}(1 + \eta_x^{p0/2}/3)/\chi_x^0(1 + \eta_x^{0/2}/3)$ is approximated by unity.

Effective reorientational correlation times τ_x^{p0} , as obtained from the linear coefficients B_x and by insertion of eq 13, 14, and 15 into eq 11, are presented in Table IV. The influence of uncondensed counterions on R_x^u leads to small corrections on the order of half the estimated experimental error margin. RbPAA data are uncorrected for this effect. However, the influence of the Rb^+ ion on the water dynamics is comparable to the effect of the Cs^+ ion and is in this context negligible.⁶ In KAc solutions the effect of the K^+ ion on the water relaxation behavior has also been neglected. The reorientational motion within the perturbed region occurs on the picosecond time scale,

Table IV
Perturbed Water Reorientational Correlation Times as Determined by the Linear Coefficients B_x

solute	$n = 15$		$n = 6$	
	τ_D^p , ps	τ_O^p , ps	τ_D^p , ps	τ_O^p , ps
HPAA		3.0 ± 0.2		4.6 ± 0.4
LiPAA	6.3 ± 0.7	5.9 ± 0.7	13 ± 2	12 ± 2
NaPAA	4.5 ± 0.3	4.4 ± 0.3	8.3 ± 0.6	8.0 ± 0.6
KPAA	4.3 ± 0.2	4.3 ± 0.2	7.7 ± 0.5	7.7 ± 0.4
RbPAA ^a	4.2 ± 0.2	4.1 ± 0.2	7.5 ± 0.4	7.4 ± 0.4
KAc ^b	3.2 ± 0.2	3.2 ± 0.2	5.2 ± 0.3	5.1 ± 0.2
NaPSS	3.7 ± 0.2	3.9 ± 0.2	6.4 ± 0.3	6.9 ± 0.3
KPSS	3.2 ± 0.2	3.4 ± 0.2	5.0 ± 0.4	5.5 ± 0.3

^aUncorrected for b_x^0 . ^bThe effect of the K^+ ion on the water dynamics in KAc solutions has been neglected.

independent of the choice of hydration number. Consequently, water molecules are not bound to the macromolecular surface. This result is in agreement with previous NMR investigations on the surface effect of, e.g., clay,⁹ silica,⁸ and PMA.² The values of τ_x^{p0} depend on the nature of the counterion as well as the polyion. This is also reflected by the relaxation behavior in the whole concentration range. These effects are discussed in the previous section.

Effective reorientational correlation times τ_D^{p0} and τ_O^{p0} are equal within the estimated experimental error margin, for all solutes studied. Hence, in the low concentration limit a possible anisotropy in perturbed water reorientational motion is not observed. This is in contrast with the reorientational motion in the vicinity of cations in simple salt solutions, in which a moderate but distinct anisotropy was observed.¹ The equality of the effective correlation times for D and ^{17}O relaxation is necessary but not sufficient to prove the reorientational motion to be isotropic. The effect of motional anisotropy may be obscured for certain orientations of the diffusion tensor, which cause an equality of the effective correlation times for D and ^{17}O relaxation.³ However, the range of these orientations is very narrow and does not include intuitively expected preferred orientations such as the molecular symmetry axis.

In solutions of the uncharged polyethylene oxide ($\text{DP} > 300$) some anisotropy of the hydration water reorientational motion was observed, even in the limit of low polymer concentration.²³ The present results for charged polymers may indicate that an average over several classes of perturbed water is observed and that exchange between these classes yields an isotropic behavior as a result of compensating effects. However, at the moment a decomposition of the perturbed water relaxation rate into contributions of charged sites and the hydrophobic backbone is not feasible.

After the discussion of reorientational correlation times and motional symmetry in the low concentration limit, the ratio of relative D and ^{17}O relaxation rates at finite concentrations is evaluated.

Finite Concentrations. As displayed in Figures 1 and 2, it may be noted that at higher concentrations deviations of the relative D and ^{17}O relaxation rates are significant. This is indicated by the quadratic coefficients, as presented in Table II. The small deviations have equal signs for all solutes studied, contrary to the situation in simple chloride solutions.¹ In simple chloride solutions the ratio of the relative D to ^{17}O relaxation rates depends on the type of cation. This was interpreted by a change in diffusion tensor properties caused by the electric field intensity on the surface of the ion. In polyelectrolyte solutions these specific counterion effects are not observed.

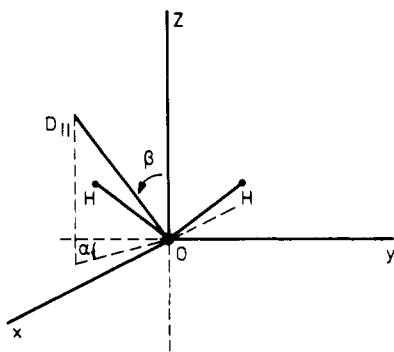


Figure 6. Definition of the orientation of the D_{\parallel} axis of the diffusion tensor with respect to the molecular frame, characterized by the angles α and β .

In PSS solutions the difference between D and ^{17}O relaxation rates is somewhat more pronounced in comparison to PAA solutions. The relaxation rates are analyzed by an axially symmetric diffusion model. The orientation of the diffusion tensor is characterized by the angles α and β , as depicted in Figure 6. According to eq 4 and 5, the ratio of D to ^{17}O relaxation rates depends on the degree of anisotropy D_{\parallel}/D_{\perp} and the orientation of the diffusion tensor with respect to the molecular frame.

To calculate the perturbed water diffusion components D_{\parallel} and D_{\perp} at any particular concentration a suitable choice of the orientation of the diffusion tensor characterized by the angles α and β has to be made. At this moment, an unambiguous choice of the orientation of the diffusion tensor is not possible, because no information is available about the structure and orientations of water molecules within the perturbed region. Therefore, exact values of the diffusion components are not calculated. However, from the ratio of D to ^{17}O relaxation a set of values for the degree of anisotropy D_{\parallel}/D_{\perp} is obtained depending on the concentration and the values chosen for α and β . No solutions are obtained for $\beta \leq 45^\circ$, for all solutes studied. The degree of anisotropy is moderate, in accordance with previously reported results of water reorientational motion in PMA solutions.² For instance, at a concentration of 4 M, the degree of anisotropy ranges from 1.2 to 10. At an equal orientation of the diffusion tensor, the anisotropy increases according to the sequences: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \sim \text{Rb}^+$ and $\text{PSS} > \text{PAA}$. However, a larger ratio of ^{17}O to D relaxation rates does not necessarily imply a larger degree of anisotropy, because the orientation of the diffusion tensor may differ. As mentioned earlier, the experimental rates include probably an average over several classes of perturbed water: regions near a charged group will differ from regions close to hydrophobic groups. The anisotropy found at high concentration should therefore not to be taken to be characteristic for "the" perturbed water molecules.

V. Conclusions

Magnetic relaxation rates of water nuclei in polyelectrolyte solutions agree with a short-range effect of the macromolecular surface on the reorientational motion of water molecules. The reorientational mobility of water molecules in the proximity of the chain decreases and

depends on the specific polyion-counterion interaction. A moderate anisotropy is observed, which vanishes in the low concentration limit. From the present results it is clear that the dynamical perturbation of water molecules near charged macromolecules is of sufficient importance to contribute to the nuclear relaxation of counterions. In a recent work on the ^{23}Na relaxation in DNA solutions a similar indication was found.²⁷ Additional experimental support for the retarded motion near a polyion and its importance for counterion relaxation was found in an investigation of ^{23}Na relaxation of Na cryptates in polyacrylic acid solutions.²⁸ In this case the enhanced ^{23}Na relaxation is solely due to the decreased reorientational mobility of the cryptate.

Registry No. PAA, 9003-01-4; PSS, 50851-57-5; H_2O , 7732-18-5; NaCl, 7647-14-5; KCl, 7447-40-7; CsCl, 7647-17-8; LiCl, 7447-41-8.

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