# On the structure and dynamics of lithium counterions in polyelectrolyte solutions: A nuclear magnetic resonance and neutron scattering study

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The structure around lithium counterions in polyacrylate solutions has been investigated by neutron diffraction, and it is concluded that small cations remain hydrated when they accumulate around a highly charged polymer. Interactions between the polyion and the counterions over a range outside the hydration shell are also observed. The relaxation rate of $^7$Li due to dipolar coupling to $^{17}$O was obtained by nuclear magnetic resonance. The results indicate that the polyion exerts a moderate influence on the reorientational dynamics of the lithium aqua-ion.

## I. INTRODUCTION

In linear polyelectrolyte solutions the counterions may be strongly attracted by the oppositely charged chain. Various descriptions exist of the resulting distribution of counterions about a cylindrical polyelectrolyte.[1-3] A common feature is the accumulation of counterions around the chain when the linear charge density parameter $\xi$ exceeds unity. $\xi$ is the ratio of the electrostatic energy between neighboring charges on the chain to the thermal energy $k_B T$,

$$\xi = e^2 / 4\pi\epsilon_0\epsilon A k_B T \qquad (1)$$

in which $A$ denotes the distance between neighboring charged beads and the other symbols have their usual meaning.

As demonstrated in a recent NMR study, this counterion accumulation has a remarkable effect on the water reorientational dynamics.[4] The solvent dynamical perturbation was found to be confined to the vicinity of the macromolecule. In this region, the water dynamics depend on the nature of both the polymeric charged side group and the counterion. In an important small angle neutron and x-ray scattering study, a monomolecular hydration layer between the charged poly(methacrylic acid) (PMA) polymer and the accumulated counterions was observed.[5] The density of this intermediate hydration water is about 8% higher than the bulk water value. Hence, to interpret the solvent dynamical behavior, the counterion short-range interaction with the surrounding water molecules and the polyion is an impor-

tant feature. In this paper, these interactions have been investigated by neutron diffraction.

The neutron scattering first-order isotopic difference method was applied to the lithium ion (i.e., $^6$Li vs $^7$Li), and the total Li$^+$ pair radial distribution function, $G_{\text{Li}}(r)$, was obtained.[6,7] $G_{\text{Li}}(r)$ yields direct information on the structural properties in the neighborhood of Li$^+$, and this function is weighted heavily in terms of the Li$^+$–water correlations [see Eqs. (3), (6), and (7)) and Table V]. Comparison of $G_{\text{Li}}(r)$ for Li–deuteroxide and Li–poly (acrylic acid) (LiPAA) facilitates a characterization of the effect of the macromolecule on the water structure around small cations. Furthermore, the use of nondeuterated or selectively deuterated macromolecules allows a more detailed analysis of short-range correlation between the cation and the polymer chain.

A second facet of this paper is the influence of linear polyions on the reorientational mobility of counterions. In a recent NMR investigation on polyelectrolytes, the small cations were included by a macrobicyclic ligand (cryptand) to form a stable counterion inclusion complex.[8] Cryptate C-13 and Na-23 relaxation showed the effect of the polyion on the reorientational mobility of these complexes to be moderate. In the present contribution, the lithium aqua-ion rotational dynamics has been investigated by $^7$Li relaxation due to dipolar coupling to $^{17}$O.

The $^7$Li nucleus relaxes partly by magnetic dipole–dipole coupling to $^{17}$O.[9,10] This contribution may be obtained by $^{17}$O enhanced $^7$Li relaxation in a series of solutions isotopically enriched in $^{17}$O. This relaxation contribution is preponderantly determined by the magnetic interaction with

TABLE I. Densities of the solutions at 300 K.

| nat LiOD | 1.141 | nat LiPAA | 1.154 | nat LiCD$_2$PAA | 1.154 |
| 6 LiOD | 1.141 | 6 LiPAA | 1.154 | 6 LiCD$_2$PAA | 1.156 |

hydration water molecules within the solvation sheath of the cation. The magnetic interaction of $^7$Li with $^{17}$O outside the hydration shell, i.e., the "outer sphere" contribution, is of minor importance.[9,10] The interaction within the aqua-ion may be modulated by overall reorientational motion of the hydration complex and/or exchange of water molecules between the hydration site and the bulk. Hence, this relaxation mechanism may elucidate those dynamical aspects of the aqua-counterion, provided the water structure around the ion is known.

## II. EXPERIMENTAL

For the neutron scattering experiments two solutions of LiOD, two solutions of LiPAA, and two solutions of D-methylene-substituted Li–polyacrylate (LiCD$_2$PAA) were prepared by weight. The lithium and, in polyelectrolyte solutions, the monomeric unit concentration was 1.21 mol/55.5 mol D$_2$O. The polyelectrolyte solutions were completely neutralized with alkali to obtain the lithium polyacrylate salts. No excess low-molecular-weight salt was present in solution. All solutions were prepared in heavy water (Aldrich, gold label quality). For each set, one sample contained natural lithium (7.4% $^6$Li and 92.6% $^7$Li), whereas the other one was prepared with $^6$Li enriched lithium (95.5% $^6$Li and 4.5% $^7$Li).

The $^6$Li enriched lithium originated from Isotec Inc., Dayton, the natural lithium from BDH chemicals Ltd, Poole. The polymers were synthesized and fractionated as described before.[11,12] The degree of polymerization (DP) was 2700 and 2500 for PAA and CD$_2$PAA, respectively. DP is determined by viscosity measurements, in the presence of 0.01 N HCl, using Mark–Houwink relations.[13] Density measurements were performed with an Anton Paar DMA 02C densitometer. The densities of the solutions are presented in Table I, the atomic concentrations are given in Table II.

The neutron scattering experiments were performed on the diffractometer 7C2, situated on the hot source of the Orphée reactor at the laboratoire Léon Brillouin, C. E. N. de Saclay. An incident neutron wavelength of 0.712 Å was selected by a Cu 111 monochromator. The scattering intensity was measured simultaneously in the total angular range ex-

TABLE III. Neutron scattering cross sections used in the correction procedures.

| Solution | Mean scattering cross section[a] (b atom$^{-1}$sr$^{-1}$) | Mean absorption cross section[b] (b atom$^{-1}$sr$^{-1}$) |
|---|---|---|
| nat LiOD | 3.81 | 0.20 |
| 6 LiOD | 3.81 | 2.52 |
| nat LiPAA | 5.45 | 0.19 |
| 6 LiPAA | 5.44 | 2.42 |
| nat LiCD$_2$PAA | 4.44 | 0.19 |
| 6 LiCD$_2$PAA | 4.43 | 2.41 |

[a] Calculated using a total cross section of 11.42 b for D$_2$O at 0.712 Å (Ref. 18).
[b] At the incident wavelength of 0.712 Å.

tending up to 128°, with angular steps equal to 0.2°, by a position-sensitive detector containing 640 cells.[14] This allowed us to reach a maximum $Q$ ( $= 4\pi \sin \theta / \lambda$, $2\theta$ diffraction angle) value of 16 Å$^{-1}$. The solutions were contained in a cylindrical vanadium can of 0.4 cm internal radius. The experiments were performed at room temperature, i.e., $300 \pm 1$ K. The measured intensities were corrected for instrumental background, container scattering, self-attenuation,[15] and multiple scattering,[16] and were placed on an absolute scale by reference to a vanadium standard.[17] The neutron scattering and absorption cross sections used in the correction procedures are listed in Table III. The corrections to the data were complicated by the high absorption cross section of $^6$Li, and certain semiempirical corrections were necessary to produce self-consistent difference functions (see the Appendix).

For the NMR studies LiPAA solutions in $^{17}$O enriched water were prepared. The concentration was 0.94 molal, both in lithium and monomeric units. The solutions were fully neutralized with natural LiOH to obtain the salts. Water isotopically enriched in oxygen was obtained from Monsanto Research Corp., containing 9.9% O-16, 51.1% O-17, and 39.0% O-18. Distilled water was deionized and filtered by a Milli-Q water purification system (Millipore Corp.) NMR tubes (homemade, quartz) were heated in a NaHCO$_3$ solution, heated in an EDTA solution, and stored for at least one week with deionized and filtered water. To remove gaseous oxygen the samples were degassed with nitrogen. Isotopic compositions of the samples are listed in Table IV.

Magnetic relaxation rates were determined on a home-modified Bruker SXP spectrometer equipped with a 6.3 T

TABLE II. Atomic concentrations of the samples prepared for neutron scattering.

| Sample | D | O | Li | Polymer atoms | | | |
| | | | | H | D | O | C |
|---|---|---|---|---|---|---|---|
| nat LiOD | 0.659 54 | 0.333 33 | 0.007 13 | ··· | ··· | ··· | ··· |
| 6 LiOD | 0.659 58 | 0.333 34 | 0.007 09 | ··· | ··· | ··· | ··· |
| nat LiPAA | 0.625 64 | 0.312 82 | 0.006 84 | 0.020 51 | ··· | 0.013 67 | 0.020 51 |
| 6 LiPAA | 0.625 72 | 0.312 86 | 0.006 83 | 0.020 47 | ··· | 0.013 65 | 0.020 47 |
| nat LiCD$_2$PAA | 0.625 72 | 0.312 86 | 0.006 83 | 0.006 83 | 0.013 65 | 0.013 65 | 0.020 48 |
| 6 LiCD$_2$PAA | 0.625 92 | 0.312 96 | 0.006 79 | 0.006 79 | 0.013 58 | 0.013 58 | 0.020 37 |

TABLE IV. Isotopic composition and Li-7 relaxation rates of 0.94 molal LiPAA solutions in O-17 enriched water.

| $p_{17}$ | $p_{18}$ | $R_{Li}(s^{-1})$ | $R_{Li}^c(s^{-1})^a$ |
|---|---|---|---|
| 0.1109 | 0.0846 | 0.493 | 0.490 |
| 0.2400 | 0.1832 | 0.502 | 0.494 |
| 0.3548 | 0.2708 | 0.514 | 0.503 |
| 0.5072 | 0.3871 | 0.531 | 0.514 |

[a] See the text. $p_{17}$ and $p_{18}$ denotes the $^{17}O$ and $^{18}O$ mole fraction, respectively.

superconducting magnet (Oxford Instruments) at the Gorlaeus laboratories, Leiden. The temperature was controlled at $298 \pm 0.5$ K with a variable temperature unit (Bruker, B-VT 1000). Lithium-7 $T_1$ relaxation times were obtained by the inversion recovery method with an estimated reproducibility of 1%. Every relaxation time represents an average over at least five measurements. FIDs were accumulated, while the relative phase of the $\pi$ and $\pi/2$ pulses was alternated.[19] The longitudinal relaxation was observed to be single exponential for all samples studied. A hundred data points were collected and a least-squares fitting procedure was used to obtain the relaxation rates. Relaxation rates are collected in Table IV.

## III. RESULTS AND DISCUSSION

### A. Neutron scattering

The total neutron diffraction pattern of a LiOD solution in $D_2O$ is a weighted average of six partial structure factors $S_{\alpha\beta}(Q)$, where the subscripts $\alpha$ and $\beta$ denote the particles involved.[6,7] The difference between the total scattering patterns for two deuteroxide solutions, identical except for the substitution $^{nat}$Li vs $^6$Li, is represented by

$$\Delta_{Li}(Q) = A\left[S_{LiO}(Q) - 1\right] + B\left[S_{LiD}(Q) - 1\right]$$
$$+ C\left[S_{LiLi}(Q) - 1\right], \qquad (2)$$

where $A = 2c_{Li}c_O b_O \Delta b_{Li}$, $B = 2c_{Li}c_D b_D \Delta b_{Li}$, $C = c_{Li}^2(b_{nat_{Li}}^2 - b_{6_{Li}}^2)$, $\Delta b_{Li} = b_{nat_{Li}} - b_{6_{Li}}$, and $c_\alpha$ is the atomic concentration of species $\alpha$ whose coherent neutron scattering length is $b_\alpha$. The numerical factors $A$, $B$, and $C$ are collected in Table V. The Fourier transform of $\Delta_{Li}(Q)$ results in a compostie radial distribution function

$$G_{Li}(r) = A\left[g_{LiO}(r) - 1\right] + B\left[g_{LiD}(r) - 1\right]$$
$$+ C\left[g_{LiLi}(r) - 1\right]. \qquad (3)$$

The scattering lengths of $^7$Li and $^6$Li have the values $-0.222 \times 10^{-12}$ and $0.20 \times 10^{-12}$ cm$^{-1}$, respectively. Consequently, the scattering constant for the Li–Li interactions, i.e., the $C$ term, is approximately zero. The difference func-

TABLE V. Scattering constants for the differences in mb.

| Sample | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| LiOD | 1.021 | 2.322 | 0 | ... | ... | ... | ... |
| LiPAA | 0.921 | 2.117 | 0 | −0.039 | 0.041 | 0.069 | ... |
| LiCD$_2$PAA | 0.918 | 2.110 | 0 | −0.013 | 0.040 | 0.068 | 0.046 |

tions, Eqs. (2) and (3), are dominated by the lithium–solvent terms, $A$ and $B$.

In the polyelectrolyte solutions, the difference structure functions take the form

$$\Delta_{Li}(Q) = A\left[S_{LiO}(Q) - 1\right] + B\left[S_{LiD}(Q) - 1\right]$$
$$+ C\left[S_{LiLi}(Q) - 1\right]$$
$$+ D\left[\overline{S}_{LiH}(Q) - 1\right] + E\left[\overline{S}_{LiO}(Q) - 1\right]$$
$$+ F\left[\overline{S}_{LiC}(Q) - 1\right] \qquad (4)$$

for LiPAA and for the selectively deuterated LiCD$_2$PAA sample, one has

$$\Delta_{Li}(Q) = A\left[S_{LiO}(Q) - 1\right] + B\left[S_{LiD}(Q) - 1\right]$$
$$+ C\left[S_{LiLi}(Q) - 1\right]$$
$$+ D\left[\overline{S}_{LiH}(Q) - 1\right] + E\left[\overline{S}_{LiO}(Q) - 1\right]$$
$$+ F\left[\overline{S}_{LiC}(Q) - 1\right] + G\left[\overline{S}_{LiD}(Q) - 1\right]. \qquad (5)$$

The Fourier transform of Eqs. (4) and (5) yields the composite radial distribution functions:

$$G_{Li}(r) = A\left[g_{LiO}(r) - 1\right] + B\left[g_{LiD}(r) - 1\right]$$
$$+ C\left[g_{LiLi}(r) - 1\right]$$
$$+ D\left[\overline{g}_{LiH}(r) - 1\right] + E\left[\overline{g}_{LiO}(r) - 1\right]$$
$$+ F\left[\overline{g}_{LiC}(r) - 1\right] \qquad (6)$$

for the LiPAA solution, and for the LiCD$_2$PAA solution:

$$G_{Li}(r) = A\left[g_{LiO}(r) - 1\right] + B\left[g_{LiD}(r) - 1\right]$$
$$+ C\left[g_{LiLi}(r) - 1\right]$$
$$+ D\left[\overline{g}_{LiH}(r) - 1\right] + E\left[\overline{g}_{LiO}(r) - 1\right]$$
$$+ F\left[\overline{g}_{LiC}(r) - 1\right] + G\left[\overline{g}_{LiD}(r) - 1\right]. \qquad (7)$$

In Eqs. (4)–(7), $\overline{S}$ and $\overline{g}$ label those terms involving the polymer. The coefficients $D$, $E$, $F$, and $G$ have the same form as the coefficients of Eq. (2), but are smaller than $A$, $B$, and $C$ as they depend on the concentration atoms in the polymer. However, they are nonnegligible, and the polymer interaction terms may provide an indication of the counterion accumulation about the cylindrical macromolecule.

The $G_{Li}(r)$'s can be interpreted directly in terms of the structure around Li$^+$. For example, where clear correlations exist between lithium and a particular atom, $\alpha$, it is a straightforward matter to obtain an interparticle distance. Furthermore, by integration over the range $r_1 \leqslant r \leqslant r_2$ of the correlation one can define a coordination number

$$n_{Li}^\alpha = \rho c_\alpha 4\pi \int_{r_1}^{r_2} g_{Li\alpha}(r) r^2 \, dr, \qquad (8)$$

where $\rho$ is the total number density of the solution.

The difference diffraction patterns are shown in fig. 1. The real space correlation functions, obtained by Fourier transformation, are displayed in Fig. 2. The $G_{Li}(r)$ functions are identical in the region of the hydration shell, i.e., $1.6 < r \leqslant 3$ Å. The first and the second peaks at distances $r = 1.97 \pm 0.02$ Å and $r = 2.51 \pm 0.02$ Å are readily assigned to Li–O and Li–D correlations, respectively. The peak areas are consistent with two deuterons per oxygen atom and a hydration number $n_{Li}^O = 4.5 \pm 0.5$. Further-
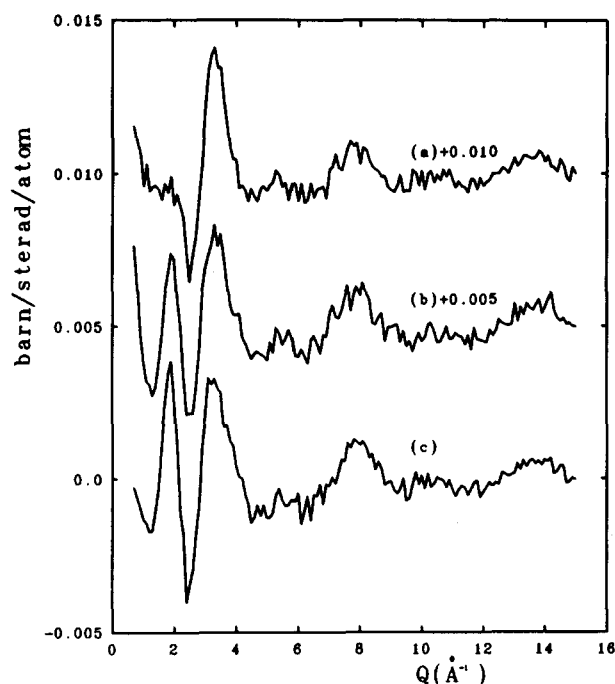
FIG. 1. First-order difference functions $\Delta_{Li}$ ($Q$) for: (a) LiOD in $D_2O$, (b) LiPAA in $D_2O$, and (c) $LiCD_2PAA$ in $D_2O$.

more, the hydration parameters are equal for all solutes studied.

Results of a neutron diffraction study of a 3.51 molal $LiCl/D_2O$ solution gave lithium hydration parameters: $r_{LiO} = 1.95$ Å, $r_{LiD} = 2.55$ Å, and $n^O_{Li} = 5.5 \pm 0.3$.[20] The distances are in excellent agreement with our results above. However, the hydration number obtained is somewhat greater. This discrepancy is probably due to uncertainties in
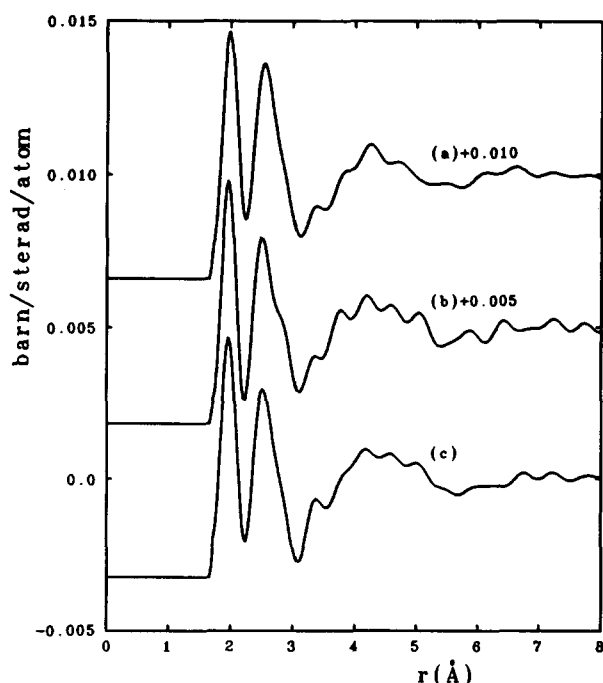


FIG. 2. The real space distribution functions $G_{Li}$ ($r$) obtained by Fourier transformation of the functions in Fig. 1. The unphysical oscillations below 1.7 Å are not shown.

correction procedures for absorption of [6]Li samples involved. In relative terms, however, because the data sets were treated in a similar manner, the results clearly indicate that the polyion does not disrupt the lithium hydration structure. A similar result was obtained for the chloride hydration in solutions of (uncharged) polyethyleneoxide.[21]

As displayed in Fig. 1, the $\Delta_{Li}$ ($Q$) functions differ significantly only in the appearance of a peak at 1.5 Å$^{-1}$ in the polyelectrolyte solutions. As discussed in the Introduction, the counterions are accumulated about the charged chain. The exact counterion distribution with respect to the backbone is unknown, but may be estimated with the simple Oosawa–Manning condensation model.[2,3] Within this simple model, the fraction of condensed counterions equals $1 - \xi^{-1}$, but in these concentrated solutions this value is probably higher. At 300 K, in a completely charged PAA solution $1 - \xi^{-1}$ equals 0.65. Hence, according to the condensation model 65% of the counterions are near the macromolecular surface. Accordingly, the feature at 1.5 Å$^{-1}$ may plausibly be associated with interactions between counterions and the macromolecular chain over a range greater than the lithium hydration. In this context, it should be noted that in the $LiCD_2PAA$ sample the sum of the scattering constants involving the polymer is twice the corresponding value in the LiPAA solution. Consequently, in the selectively deuterated polymer solution the peak at 1.5 Å$^{-1}$ is more pronounced.

The lithium–polyion interaction contribution is not resolved in the composite radial distribution function. This is probably due to the limited signal-to-noise ratio in the region beyond 4 Å, and/or the distribution width. Although the information is, in principle, available, it is desirable to extend the momentum transfer range of our experiment to a wider range of $Q$. In principle, it is possible to separate the cation–polymer interaction by performing a second-order difference experiment.[22] However, such a study is beyond the limits of present day technology.

In this first experimental determination, the neutron scattering results show clearly that the cation–water complex remains intact in the presence of a linear highly charged polymer. The results indicate interactions between the cation and the polymer chain, but at distances outside the hydration shell. These conclusions are in accordance with the results of the lower resolution neutron and x-ray scattering studies by Plestil *et al.*[5] As discussed in the Introduction, they concluded that the counterions are separated by a monomolecular hydration layer from the polymer. The present neutron results strongly suggest that these intermediate water molecules are still coordinated to the cation.

## B. Nuclear magnetic relaxation

No field dependence of the [7]Li relaxation due to dipolar coupling to water [17]O atoms was observed. Hence, the [17]O dipolar interaction contribution to the [7]Li relaxation is given by[9,10]

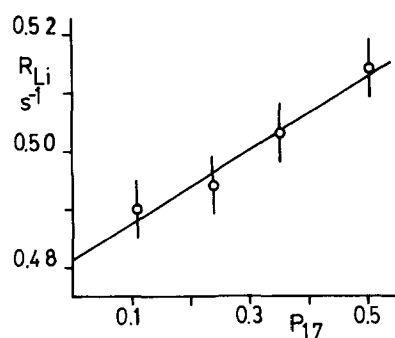$$R^c_{LiO} = R^{com}_{LiO} + \delta_{Li} \qquad (9)$$

with

FIG. 3. Li-7 relaxation rate vs the O-17 mole fraction in 0.94 molal LiPAA solutions. The line is drawn according to the linear least squares fit: $R_{Li}^c = (0.481 \pm 0.003) + P_{17}(0.062 \pm 0.008)$.

$$R_{LiO}^{com} = \frac{35}{3} \gamma_{Li}^2 \gamma_O^2 h^2 \tau_c N_O \pi^{-1} \int_0^d \frac{g_{LiO}(r)}{r^4} dr. \quad (10)$$

In Eq. (9), the lithium relaxation rate is understood to be corrected for $^{17}O$ and $^{18}O$ isotope effects on the viscosity of the solvent. This is explicitly indicated by the superscript $c$ for $R_{LiO}^c$ only. $R_{LiO}^{com}$ is the contribution to the relaxation rate originating from the hydration shell; $\delta_{Li}$ is the bulk water contribution to the rate. The latter contribution will be discussed below. In Eq. (10), the integral has to be evaluated over the region of the first interaction peak in the radial distribution function $g_{LiO}(r)$. The oxygen atom number density is denoted by $N_O$, $\tau_c$ denotes the correlation time, and the other symbols have their usual meaning.

The $^7Li$ relaxation rates in $^{17}O$ enriched solutions are collected in Table III. Oxygen isotope effects on the correlation time are expected to be proportional to the effects on the viscosity of the solvent. The linear correction (10) in Ref. 23 is applied. Relaxation rates corrected for these effects are also collected in Table III. Figure 3 displays the corrected lithium relaxation rates vs the $^{17}O$ mole fraction. In view of the observed linearity, one has

$$R_{Li}^c = R_{Li}(p_{17} = 0) + p_{17}R_{LiO}^c, \quad (11)$$

where $R_{Li}(p_{17} = 0)$ is the background contribution due to $^7Li$ quadrupolar and Li–H dipolar relaxation. This background contribution is not considered here. From the fit of Eq. (11) to the data displayed in Fig. 3, one has: $R_{LiO}^c = 0.062 \pm 0.008 \text{ s}^{-1}$.

To allow an evaluation of the correlation time $\tau_c$, the "outer sphere" contribution $\delta_{Li}$ has to be estimated. In LiCl solutions, $\delta_{Li}$ equals 10% of the total $^7Li$–$^{17}O$ dipolar interaction contribution.[9] This figure has been evaluated on the basis of the translational diffusion model for the relative motion of ions and bulk water molecules. In polyelectrolyte solutions, the outer sphere contribution is difficult to estimate, due to the restricted mobility of ions and water near the macromolecular surface.[4,8,24] Therefore, as an approximation, $\delta_{Li}$ is taken to be 10% of the total rate, as it is in a simple electrolyte solution. In the neutron composite radial distribution function $G_{Li}(r)$, the first peak originates from Li–O interactions. Hence, in the region of this first interaction peak, the function $g_{LiO}(r)$ can be evaluated directly from the composite function $G_{Li}(r)$. With Eqs. (9) and

(10), after integrating $G_{Li}(r)/r^4$ over the region of the first peak (i.e., up to 2.23 Å) and subtracting $\delta_{Li}$, one obtains $\tau_c = 43 \pm 7$ ps. To obtain an upper limit, the outer sphere contribution may be neglected. In this case $\tau_c$ takes the value $48 \pm 8$ ps. Correlation times are understood to be averaged over the distribution with respect to the polyion.

The correlation time $\tau_c$ may be expressed in terms of the overall reorientational correlation time of the total hydration complex $\tau_{ov}$, and the exchange time $\tau_{ex}$,

$$\tau_c = \frac{\tau_{ov}\tau_{ex}}{\tau_{ov} + \tau_{ex}}. \quad (12)$$

The correlation time $\tau_{ex}$ characterizes the exchange of the water molecule between the hydration site and the bulk. The direction of the principal axis of the magnetic dipole–dipole interaction tensor coincides with the Li–O axis. In consequence, internal motion about this axis is not able to modulate this interaction.

In a simple salt solution, the corresponding $^7Li$–$^{17}O$ dipolar interaction correlation time has been reported to be 17.5 ps.[9] The value of the overall reorientational correlation time is approximately 25 ps. The latter value has been estimated on the basis of the size of the aqua-ion (according to the hydrodynamic Stokes–Einstein relation) and/or the experimental results on paramagnetic divalent ions.[9] Accordingly, the $^7Li$–$^{17}O$ dipolar interaction correlation time and the overall reorientational correlation time are of the same order of magnitude. In consequence, in simple salt solutions, it is not clear whether the exchange mechanism has to be taken into account.

The reorientational correlation time of a cryptate counterion in a 0.35 molal polyacrylate solution equals $64 \pm 4$ ps.[8] This figure compares favorably with the value of $\tau_c$ and suggests the exchange mechanism to be of minor importance. When comparing these data, one must take into account a difference in radii between these complexes. The radius of the cryptate complex equals 3.5 Å, whereas the radius of the lithium aqua-ion is 3 Å. The latter value has been estimated from the relevant minimum in the radial distribution function displayed in Fig. 2. Hence, in the polyacrylate solution, the experimental correlation time $\tau_c$ may be identified with the overall rotational correlation time of the hydration complex $\tau_{ov}$.

The relatively moderate value of the reorientational correlation time indicates a modest influence of the polyion on the reorientational mobility of the lithium aqua-ion. This conclusion is in accordance with the NMR results on the cryptate counterion inclusion complexes.[8] Site binding can be excluded, since this would cause a dramatic reduction in reorientational mobility. This is also supported by the neutron diffraction results, which do not show a change of both the hydration number and molecular orientation within the hydration sphere.

If the exchange mechanism contributes to the modulation of the $^7Li$–$^{17}O$ dipolar interaction, the resulting value of the overall correlation time increases. For instance, if $\tau_{ex} = \tau_{ov}$ these correlation times take the value $2\tau_c$, i.e., 86 ps. Indeed, in simple salt solutions, the exchange mechanism has been taken into account to explain the relatively low

value of the correlation time for rotational motion of the Li–H vector.[25] It should be noted that the Li–H dipolar interaction is also modulated by internal motion of a water molecule about the Li–O axis. Hence, the latter relaxation mechanism is less suitable to investigate the hydration complex overall reorientational motion compared to the Li–$^{17}$O dipolar interaction. In the limiting situation, $\tau_{ex}$ equals $\tau_c$ and $\tau_{ov} \gg \tau_{ex}$. Although this value of the exchange correlation time is not unrealistic, the long overall correlation time seems not to be compatible with the results obtained from the cryptate counterions in polyacrylate solutions. However, a situation in which both exchange and overall reorientational motion contribute to the modulation of the dipolar interaction between $^7$Li and $^{17}$O cannot be excluded.

## IV. CONCLUSIONS

The neutron diffraction results show clearly that counterions remain hydrated when they accumulate near a highly charged linear macromolecule. Interactions between the polymer and the counterions are indicated, although the present experimental accuracy and momentum transfer range do not allow a detailed analysis of the counterion distribution with respect to the chain. These results emphasize the importance of the specific polyion–counterion interaction for the interpretation of the solvent reorientational dynamics in the proximity of the macromolecular surface. An NMR study of water dynamics in polyelectrolyte solutions gave similar results.[4]

The interpretation of $^7$Li relaxation due to dipolar coupling to $^{17}$O is complicated by effects involving the exchange of water molecules between the hydration site and the bulk. However, for a coherent interpretation of this relaxation mechanism and the NMR results on cryptate counterions, it is strongly suggested that the exchange contribution is of minor importance. The influence of the polyion on the counterion reorientational mobility is moderate. This result supports the absence of site binding of the counterion to the macromolecular chain. This is also indicated by the neutron diffraction radial distribution functions which do not show inner hydration sphere complex formation of the lithium ion and the polymeric charged group.

## ACKNOWLEDGMENTS

## APPENDIX

Neutron first-order differences were obtained by direct subtraction of the normalized structure functions for solutions containing natural lithium and lithium enriched in Li–
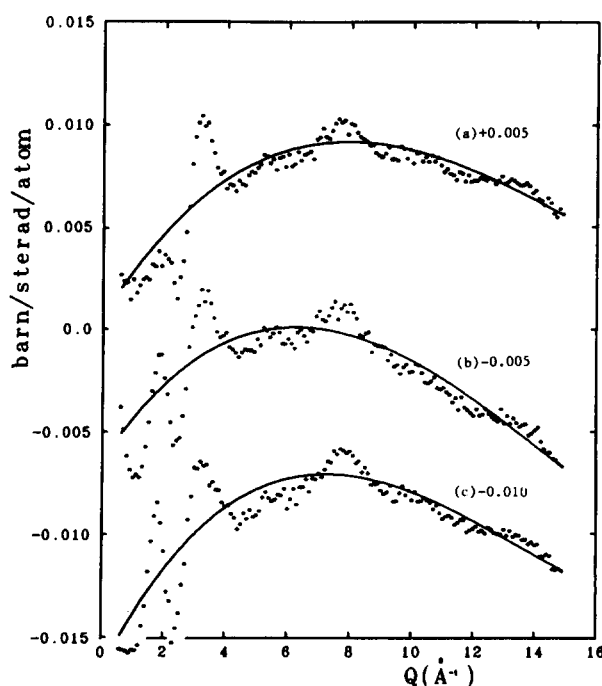


FIG. 4. First-order difference functions $\Delta_{Li}(Q)$ (points) obtained by direct subtraction of the corrected total scattering patterns, and cubic splines fitted to these (solid lines). (a) LiOD in $D_2O$, (b) LiPAA in $D_2O$, and (c) LiCD$_2$PAA in $D_2O$.

6, respectively, and are shown in Fig. 4. It should be noticed that there is a characteristic bend in each difference function, which is most pronounced in the case of the solution containing the most hydrogen. These bends are thought to originate from the approximations used in the scattering corrections, which result in the incomplete cancellation of the "self"-scattering terms in the difference function, when a highly absorbing isotope is used in the presence of light atoms. A significant distortion of the "distinct" scattering terms, which contain the structural information, is not expected.

The effect of these residual self terms is to introduce a large amount of oscillations in the Fourier transform, and so it is necessary to correct the data sets. To make any rigorous correction would require a detailed knowledge of $S(Q,\omega)$ for each solution. However, one can make a semiempirical correction, using the fact that $\Delta_{Li}(Q)$ should oscillate about zero for large $Q$.

In order not to bias the results, and to allow a direct comparison between the different data sets, a single cubic spline was fitted to each difference function. A least-squares fitting procedure was used. The fit to each set of data is shown in Fig. 4. The spline fit was then subtracted to obtain the difference functions shown in Fig. 1.

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