Hydration of Chloride Ions in a Polyelectrolyte Solution Studied with Neutron Diffraction

T. W. N. Bieze,[†] R. H. Tromp,[§] J. R. C. van der Maarel,[†] M. H. J. M. van Strien,[†]
M. C. Bellissent-Funel,[⊥] G. W. Neilson,[‡] and J. C. Leyte*,[†]

Department of Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands, H. H. Wills Physical Laboratory, Bristol University, Royal Fort, Tyndall Avenue, Bristol BS 1TL, U.K., Cavendish Laboratory, University of Cambridge, Madingly Road, Cambridge CB3 0HE, U.K., and Laboratoire Leon Brillouin (Laboratoire commun CEA-CNRS), CEN-Saclay, 91191 Gif sur Yvette Cedex, France

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A neutron diffraction isotopic substitution experiment was carried out on the chloride ion in an aqueous solution of the polybase linear poly(ethylenimine) and DCl at high polymer charge density. The composite radial distribution function of all atomic species about Cl^- ($G_{Cl}(r)$) is compared with that of Cl^- in a low molecular weight salt solution, and with that in a solution of the nonionic polymer poly(ethylene oxide). For the first time, it is observed that the presence of a linear polyion seriously affects $G_{Cl}(r)$ in an r-space region commonly referred to as the first hydration shell. This observation is suggestive of close contact between polyelectrolyte and counterion. The nuclear magnetic relaxation rate of Cl^- is strongly enhanced in the presence of the polycation, and it is concluded that an increase in the coupling constant may at least be partly responsible for the observed NMR effect.

Introduction

The interaction of counterions with charged macromolecules such as linear polyelectrolytes remains a topic of fundamental interest. In general, a high linear charge density will result in an accumulation of counterions around the chain. Direct evidence for counterion clustering around cylindrical micelles was obtained by Chen *et al.*[1] using SAXS and SANS. The radial dimension of the counterion cloud around the charged micelles decreases rapidly as a function of increasing charge density. In 150 base pair DNA[2] fragments as well as in polystyrene sulfonic acid solutions,[3] the counterion distribution was studied using low-resolution SANS in the q range $0.02 \leq q \leq 0.35$ Å^{-1}. It was shown that the results are consistent with the counterion radial distribution profile given by the Poisson-Boltzmann equation together with the cell model.[4] Corresponding high-q diffraction data showing the consequences of counterion accumulation in the close neighborhood of the chain (1-10-Å region) are, however, scarce.

For cylindrical polyions the radial distribution of the counterions can be described in terms of the Poisson-Boltzmann equation together with the cell model.[4] Solutions to more detailed models have also been presented.[5] These solutions generally show a smoothly decreasing counterion concentration profile as they move away from the polyelectrolyte axis. Alternatively, one has condensation models, i.e., two-phase models in which part of the counterions are thought to be condensed. Within the framework of condensation models, different ideas exist about the condensed counterions. In the description offered by Manning and Oosawa,[6,7] condensed ions retain their translational freedom, while other models[8-10] suggest that a fraction of the counterions are bound to the polyelectrolyte backbone. Binding constants are introduced in the latter group. In general, condensation models do not predict profiles describing the radial counterion distribution.

Little is known about the short-range counterion-polyion structure in the immediate vicinity of the polymeric backbone. Various models may be envisaged: Close proximity between the interacting charges may preclude solvent molecules from occupying the interstitial site (contact ion pair). Alternatively, less close contact between oppositely charged species may provide space for one or more solvent molecules (solvent-separated ion pair). Accordingly, the counterion-polyion interaction is expected to influence both the amount and the distribution of water hydrating the interacting species.

The fate of this hydration water is still a subject of contention,[11,12] the matter being especially relevant to the interpretation of nuclear magnetic relaxation rates of counterions. In aqueous polyelectrolyte solutions, the relaxation of ions bearing a nuclear quadrupole moment, such as Cl^-, Na^+, and Li^+, is enhanced in comparison to low molecular weight salt solutions. Relaxation rates are sensitive to the magnitude of electric field gradient(s) and their temporal behavior. Changes in either of the aforementioned quantities may be responsible for the relaxation rate enhancement observed in polyelectrolyte solutions. Knowledge of the extent to which the symmetry of the hydration sphere of the ion is disturbed by the polarizing effect of the nearby polyions and/or by association is of importance in understanding the origin of the observed NMR effects.

Neutron diffraction, combined with isotopic substitution (NDIS),[13,14] allows for the determination of $G_i(r)$, the radial pair correlation function of all atomic species around atom i. If atom i represents an ion, this technique can be used to obtain information on the organization of water in the first hydration shell. It can therefore directly measure a polyion's influence on the spatial and orientational distribution of molecules in the immediate surroundings of the ion. Consequently, comparison of the hydration sphere of an ion in the presence of polyions with the situation in low molecular weight salt solutions enables one to investigate whether the effect of polyions on the magnetic relaxation of counterions involves a structural perturbation of the ionic hydration shell.

Earlier applications of NDIS on (counter)ions in polymer and polyelectrolyte solutions have shown that the direct molecular environment of the ion is essentially unaffected by the presence of the macromolecule: Both $G_{Li}(r)$ of Li^+ in poly(acrylate) (PAA) solution[15] and $G_{Cl}(r)$ of Cl^- in a solution of the nonionic poly(ethylene oxide) (PEO)[16] show that the first hydration shells of the respective ions are similar to the situation in the corresponding low molecular weight salt solutions. The aim of the present work

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* To whom correspondence should be addressed.
[†] University of Leiden.
[‡] Bristol University.
[§] University of Cambridge.
[⊥] Laboratoire Leon Brillouin.
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TABLE 1: Scattering Prefactors in $\Delta_{Cl}(q)$ of 1.5 m LPEI/DCl, 3.62 m NaCl, and 2 m PEO Solution in 3.62 m NaCl[a]

	prescattering coefficients (mb)							
	A (D_w)	B (O_w)	C (Cl)	D (H_p)	E (N_p)	F (C_p)	G (D_p)	H (Na)
LPEI	6.4	2.7	0.1	−0.2	0.1	0.2	0.2	
NaCl	11.65	5.06	0.42					0.23
NaCl/PEO	9.69	4.39	0.34	−0.45		0.40		0.19

[a] Prefactors A–G are defined in eq 4. Prefactor H is only relevant to solutions containing sodium. All solutions are prepared with heavy water. Subscripts w and p refer to water and polymer, respectively.

is to investigate the hydration of Cl^- in a solution of fully neutralized linear poly(ethylenimine) (LPEI). The results will be compared with the aforementioned results, as well as with data from a low molecular weight salt solution (NaCl[16]). Due to the fact that poly(ethylenimine) bears the positive charges directly on the backbone, the aqua environment of the weakly hydrated counterion (Cl^-) may be more severely affected than was observed on previous occasions.

Experimental Section

Linear poly(ethylenimine) (LPEI) is a polymer with repeat unit $-(CH_2CH_2ND)_n-$ (in a heavy water solution). With the addition of DCl, the secondary amine groups are protonated to $-ND_2^+-$. LPEI was obtained via a cationic ring-opening polymerization of 2-phenyl-2-oxazoline followed by acid-catalyzed debenzoylation of the chain. The gist of this synthetic route[17] is that the nitrogen in the ring is protected, thereby reducing side reactions (e.g. cross-linking) once the chain has been formed. The molecular weight was determined with GPC: $M_w = 15\,000$ g mol^{-1} ($M_w/M_n = 2$). Freeze-dried polymer material was dissolved in H_2O, and a sample with excess added KNO_3 was titrated with HCl to determine the monomer concentration. The LPEI solution was divided into equal parts. One half was completely neutralized with $H^{35}Cl$ solution and the other half with $H^{37}Cl$ solution. Both LPEI/DCl solutions were freeze-dried and dissolved in D_2O, and this process was repeated six times. In the final exchange, D_2O was added gravimetrically to obtain two identical LPEI/DCl/D_2O solutions of 1.5 monomolal LPEI and Cl. The concentration of the solutions was confirmed with the aid of a carbon analyzer (Ionics 1555B). The density of the 1.5 monomolal LPEI/HCl was found to be 1063(±2) kg/m^3. On the assumption that the atomic number density, 0.094 atoms/Å^3, was unchanged under H/D substitution of the solvent, the density of the 1.5 monomolal LPEI/HCl was calculated to be 1171(±2) kg/m^3.

The neutron diffraction experiments were carried out on the 7C2 spectrometer situated on the hot source of the Orphée reactor at the Laboratoire Léon Brillouin. The sample container was cylindrical with a diameter of 6 mm and was made of vanadium of 0.1-mm thickness. Absolute intensities were obtained by normalization to the scattering from a vanadium rod. Attenuation and multiple scattering corrections were performed according to refs 18 and 19, respectively. During the experiment the sample was kept at ambient temperature (22 °C).

NMR experiments were performed on a home-built spectrometer equipped with a 6.3-T magnet (Oxford Instruments) at 25 °C. From the samples used for NMR experiments, paramagnetic impurities in LPEI were removed by means of ligand extraction with EDTA[20] (Triplex III, Merck). $ZnCl_2$ (Merck, PA) and $BaCl_2$ (Merck) were used without further purification. All water was filtered using a Milli-Q installation (Millipore Corp.). NMR samples were flushed with nitrogen to remove oxygen gas. Spin lattice relaxation rates were determined using the phase-alternating inversion recovery method (π-τ-$\pi/2$).

Neutron Diffraction and Isotropic Substitution (NDIS)

The NDIS method has been described in detail elsewhere (see e.g. refs 21 and 22). Therefore only a short outline will be given. NDIS is based on the fact that isotopes of the same element behave chemically identically but have different neutron scattering lengths. The coherent part of the differential cross section of a multicomponent system is given by

$$\frac{d\sigma}{d\Omega} = \sum_{ij} b_i b_j c_i c_j [S_{ij}(q) - 1] \qquad (1)$$

where c_i and b_i are the atomic fraction and the bound coherent neutron scattering length of atomic species i, respectively, $S_{ij}(q)$ denotes the partial structure function of the species i and j at the momentum transfer $\hbar q$. When the difference is taken between the differential scattering cross sections of the two identical systems, differing only in the isotope of one of its constituents, the difference function

$$\Delta_i(q) = \sum_j C_{ij}[S_{ij}(q) - 1] \qquad (2)$$

is obtained, where C_{ij} are the scattering prefactors

$$C_{ij} = 2c_i c_j b_j (b_i - b_{j}) \qquad (i \neq j)$$

and

$$C_{ij} = c_i^2 (b_i^2 - b_{i'}^2) \qquad (i = j)$$

where $b_{i'}$ is the scattering length of the newly introduced isotope. The radial distribution function $G_i(r)$ results from the Fourier transform of the difference function $\Delta_i(q)$:

$$G_i(r) = (1/2\pi^2 \rho r) \int_0^\infty \Delta_i(q)\, q \sin(qr)\, dq \qquad (3)$$

$G_i(r)$ is the composite radial distribution function of all atomic species around an atom of species i. In terms of the partial correlation functions $g_{ij}(r)$ of an LPEI/DCl solution in D_2O one has

$$\begin{aligned} G_{Cl}(r) = {} & A[g_{ClD_w}(r) - 1] + B[g_{ClO_w}(r) - 1] + \\ & C[g_{ClCl}(r) - 1] + D[g_{ClH_p}(r) - 1] + E[g_{ClN_p}(r) - 1] + \\ & F[g_{ClC_p}(r) - 1] + G[g_{ClD_p}(r) - 1] \end{aligned} \qquad (4)$$

where subscripts w and p refer to water and polymer, respectively, and the factors A–G represent the scattering prefactors. Since $A,B \gg C,D,E,F,G$, the method basically yields a distribution function in which $g_{ClD_w}(r)$ and $g_{ClO_w}(r)$ are heavily weighted. The prefactors are collected in Table 1, together with those from a 3.62 m NaCl solution and a 2 m PEO solution in 3.62 m NaCl.

Results and Discussion

Figure 1 shows the difference scattering patterns obtained from three aqueous solutions in which the chloride ion was isotopically substituted. In order to compare the difference functions of solutions at different concentrations, all data are multiplied by a factor $4\pi\rho c_{D_w} A^{-1}$; i.e. they are normalized to the Cl–D correlation which produces the largest signal in $\Delta(q)$. The top line (full curve) in Figure 1 shows the $\Delta(q)$ for a 1.5 monomolal LPEI/DCl solution, LPEI being fully neutralized by DCl. The other curves correspond to NaCl and NaCl/poly(ethylene oxide) (PEO)

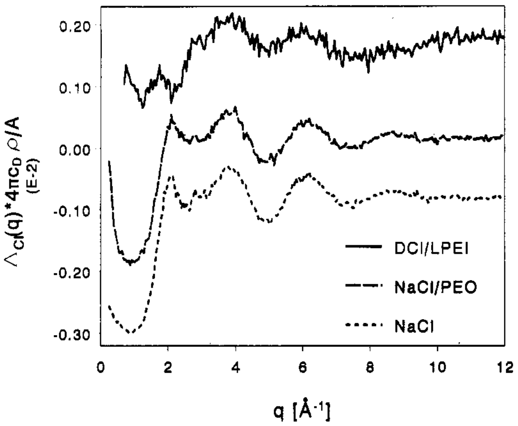

Figure 1. $\Delta_{Cl}(q)$ in a 1.5 monomolal LPEI/DCl solution in D_2O, a 2 m PEO solution in 3.62 m NaCl, and a 3.62 m NaCl solution. For the sake of comparison, all curves are normalized to the signal due to the Cl–D correlation (i.e., multiplied by $4\pi\rho c_{D_w}A^{-1}$).

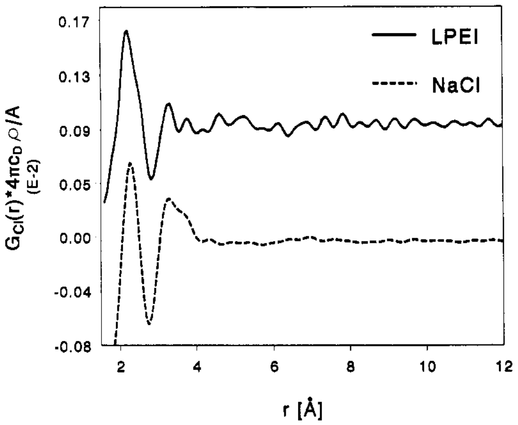

Figure 2. Radial distribution function $G_{Cl}(r)$ in 1.5 monomolal LPEI/DCl and a 3.62 m NaCl solution. All solutions are prepared in D_2O. All curves are multiplied by $4\pi\rho c_{D_w}A^{-1}$.

solutions (see legend). The two latter data sets are similar, differing only in the lower q region ($q < 1$ Å^{-1}). A comparison of these functions with the LPEI data reveals clearly that the polyion induces more pronounced changes in $\Delta(q)$. A more detailed discussion of $\Delta(q)$'s will follow.

Real space correlation functions, obtained by Fourier transformation (eq 3) of the difference, are displayed in Figure 2. Structure at a distance less than 1.6 Å from the Cl^- nucleus was considered to be unphysical and was therefore suppressed. It was checked that back-transformation of $G_{Cl}(r)$ is, within statistical error, the same as the experimentally observed difference function. The difference between the low-q regions in $\Delta_{Cl}(q)$ from the NaCl and the NaCl/PEO solutions will affect nonresolved broad features in $G_{Cl}(r)$. Accordingly, only $G_{Cl}(r)$ from NaCl is shown in Figure 2. The $G_{Cl}(r)$ from the LPEI solution (full curve) shows one prominent feature at 2.3 Å. This feature is due to correlations between the D atoms of the hydration water and the Cl^- ion.[23] The distance of closest approach between Cl^- and D is in accordance with results from other low molecular weight salt solutions[24] in which the first feature was always found in the 2.22–2.29-Å range. Since there is a clear correlation, one obtains the coordination number $\bar{n}_{Cl}^{D}$ by integrating this peak according to

$$\bar{n}_{Cl}^{D} = 4\pi\rho c_{D_w}A^{-1}\int_{r_1}^{r_2} G_{Cl}(r)\, r^2\, dr \qquad (5)$$

where ρ is the atomic number density and A is the scattering prefactor for deuterium in the solvent. Taking r_1 and r_2 as 1.6 and 2.8 Å, respectively, one calculates 6.5(±0.4) D atoms surrounding a Cl^-. Although this figure is slightly larger than

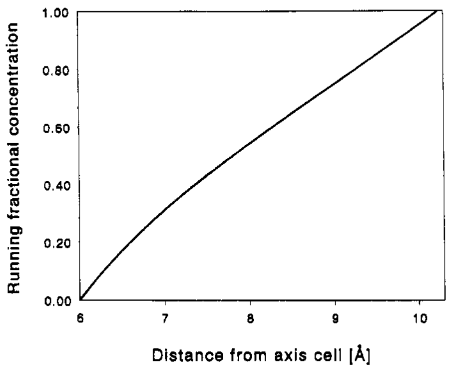

Figure 3. Fraction of Cl^- enclosed in a cylindrical cell as a function of the distance from the cell axis in a 1.5 m LPEI/DCl solution. The polymer is assumed to be a straight, homogeneously charged chain, the distance of closest approach between polyelectrolyte and counterion being 6 Å.

the conventional value for Cl^- hydration (5.2–6.3), it is not believed to be significantly different from previous findings.[24] Except for a minor feature at 3.3 Å, no further significant structure is observed in $G_{Cl}(r)$.

In most NDIS experiments on aqueous Cl^- solutions, a second peak is observed between 3.5 and 4.5 Å. This feature is clearly seen in $G_{Cl}(r)$ from a 3.62 m NaCl heavy water solution (Figure 2, dashed line). It was shown[23] to result from the correlation with the O atom and the second D atom of a coordinated D_2O molecule. In such cases the first hydration sphere of a Cl^- ion is composed of six water molecules, touching the ion with one D atom, while the other D atom is in the outer region of the first hydration shell. A similarly shaped $G_{Cl}(r)$ has been obtained using a wide range of counterions: Li^+,[25] Na^+,[16] Ba^{2+},[25] Ca^{2+},[26] Ni^{2+},[22] Cu^{2+},[27] Nd^{2+},[25] and TMA^+.[28] The exact shape, size, and position of the two main features in $G_{Cl}(r)$ are only slightly dependent on the nature and concentration of the counterion. Accordingly, the NaCl data may be used to calculate the average geometry of water molecules in the aqua–Cl ion in the case of non-ion-pairing ionic solutions.

In the present system of LPEI and DCl, however, the second peak is not observed. One may therefore conclude that the presence of the polyion LPEI has a significant effect on an r-space region in $G_{Cl}(r)$ which is usually designated as the first hydration shell. This distortion is most likely caused by the interaction between LPEI and Cl^-.

The counterions in a solution containing a highly linear charged polyelectrolyte are dispersed over a range of radial distances from the polyelectrolyte chain. The $G_{Cl}(r)$ under discussion is an average of the Cl^- at all distances. In order to assign positively the cause of a distortion of $G_{Cl}(r)$ to the presence of the polyelectrolyte chain, it is essential that a sufficient fraction of the Cl^- ions are within a certain—small—distance from the polyion. An estimate of the local concentration close to the polyelectrolyte chain can be obtained from the Poisson–Boltzmann equation solved for the cylindrical case.[4] From known bond angles and bond lengths, the average monomer length in LPEI was estimated to be 3.4 Å. If the most closely associated counterions retain their hydration shell, the minimal approach distance between the center of the counterion and the axis of the cylindrical cell is taken to be 6 Å. In Figure 3 the running (fractional) concentration has been plotted as a function of the distance to the cell axis. It is seen that approximately 80% of the counterions reside in a shell around the polyion having a thickness equal to the radius of a hydrated ion. If the hydration shells of this fraction were to be affected by LPEI, then this fraction is sufficiently large to produce a noticeable effect in $G_{Cl}(r)$.

In the following paragraphs a number of polyion–counterion configurations are discussed which could cause a distortion in $G_{Cl}(r)$. Figure 4 serves as an illustration. The main difference between the configurations is the distance between the polyelectrolyte and the counterion.

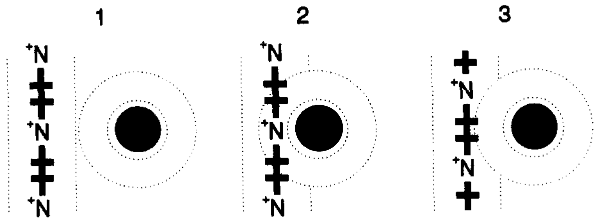

Figure 4. Number of polyelectrolyte–counterion configurations which may induce a perturbation of the primary hydration sphere of the counterion (Cl^-). Boundaries of hydration layers are indicated with dashed lines.

One may suggest a configuration in which the polyelectrolyte and counterion stay rather remote (Figure 4.1), and contact is made only between the hydration sheaths of the interacting species. This may result in a broader spatial and orientational distribution of Cl^- hydration water. Since the atoms within a D_2O molecule are highly correlated, this modified distribution will affect *all* parts of $G_{Cl}(r)$ concerned with the first hydration shell. This may explain why not only the signal in the 3.5–4.5-Å range (outer D and O) is affected but also the signal at 2.3 Å (inner D) is slightly broadened and the minimum at 2.7 Å has become more shallow when compared to $G_{Cl}(r)$ from an NaCl solution.

Alternatively, one could assume direct association of Cl^- to an $-ND_2^+-$ site on LPEI. This configuration is shown in Figure 4.2. It bears a resemblance to a contact ion pair and may be expected to bring about important changes in $G_{Cl}(r)$. Since the polyelectrolyte and counterion are very close in this conformation, 20% of the volume of the first hydration shell is excluded for the D_2O molecules by the van der Waals envelope of the macromolecule. The consequential dehydration of the first hydration shell would be expected to result in a smaller signal at 2.3 Å in $G_{Cl}(r)$. Since six D atoms are counted nevertheless, this reduction could be compensated, possibly by the deuteron(s) from the quaternary ammonium ion. In aqueous ammonia solutions (NH_4OH), where the N^+ is readily accessible for the Cl^- ion, ion-pairing is not observed.[29] Similarly, in tetramethylammonium (TMA) solutions, $G_{Cl}(r)$ is unperturbed[28] by the ammonium ion. Although the latter examples do not refer to polyion solutions, they are relevant to the present discussion, for they illustrate that N^+ and Cl^- are not especially prone to ion-pairing. Interestingly, a polyion–counterion configuration bearing resemblance to the one suggested in Figure 4.2 has previously been proposed[30] to explain the X-ray diffraction pattern observed from the extremely stable (solid state) stoichiometric LPEI/HCl complex. Accordingly, direct association of Cl^- to LPEI cannot be excluded, although it is considered to be an unlikely option.

As a third possible cause, one may suggest contact between the bare polyelectrolyte chain with the outer regions of the hydrated ions. Correlations between Cl^- and the polymer hydrogens now become observable in the $3.5 \leq r \leq 4.5$ Å region (Figure 4.3). Since ^1H has a negative scattering length, $Cl-^1H$ correlations can introduce negative additive contributions to $G_{Cl}(r)$. Correlations with polymer protons may thus reduce the signal normally observed here. Since the fractional concentration of the polymer protons (H_p) is small compared with that of water deuterons and oxygen (D_w and O_w), the option argued here can only form an explanation for the reduction in intensity in the 3.5–4.5-Å region in $G_{Cl}(r)$ if Cl and H_p are highly correlated.

Although it is concluded that $G_{Cl}(r)$ is perturbed by the polyion, it is stressed that on the basis of $G_{Cl}(r)$ alone, no firm assessment can be made regarding the precise nature of the distortion.

Intermediate Scattering Regime. In previous NDIS experiments on (counter)ions in poly(acrylic acid) (PAA) and poly(ethylene oxide) (PEO) solutions, it has been shown that, although the polymer comes close to the ion, it does not enter the first hydration shell. Strong evidence for this is given in ref 15 where NDIS on the lithium ions was carried out in D_2O solutions of LiOD, Li–CH_2PAA, and Li–CD_2PAA. Although the Li–polyion correlation is not resolved in $G_{Li}(r)$, comparison of the intermediate q range (0.5–2 Å) of $\Delta(q)$ from LiOD and LiPAA solutions shows that the polymer introduces a peak in this q region. These features indicate correlations spanning further than the first hydration shell. The amplitude of this peak was shown to be dependent on the isotropic nature of the polymer, thereby conclusively linking these features in $\Delta(q)$ to counterion–polyion correlations.

Long-range polymer–ion interactions are also observed in a poly(ethylene oxide)/NaCl solution. Comparison of the lower two difference functions in Figure 1 shows that addition of the nonionic polymer to an NaCl solution causes a significant increase in the lower q region of $\Delta(q)$. At higher q values, the difference functions are essentially identical. In ref 16 it is shown that the low-q feature in the $\Delta_{Cl}(q)$ resulting from PEO is not resolved in $G_{Cl}(r)$.[6] Accordingly, it was concluded that, in aqueous solution, PEO does not perturb the primary hydration shell of the Cl^- ion. In spite of the weaker S/N ratio, it is evident that LPEI extends its influence to higher q values in $\Delta_{Cl}(q)$ than does PEO; e.g., the feature at 2.1 $Å^{-1}$ is absent in the LPEI/DCl solution. Even at higher q values ($q > 2.5$ $Å^{-1}$), the general shape of $\Delta_{Cl}(q)$ differs from the corresponding function obtained from the low molecular weight salt solution. Accordingly, changes in $G_{Cl}(r)$ may be expected to occur at lower r values than was observed in the NaCl and PEO/NaCl solutions.

The reason PEO and PAA are incapable of disturbing the primary hydration shells of Cl^- and Li^+, respectively, is qualitatively understood: Since PEO is uncharged, the polymer–ion interaction is weak and, accordingly, cannot severely affect the Cl^- hydration shell even though the Cl^- ion is but weakly hydrated. Conversely, in the Li/PAA system, the interaction is expected to be stronger, but now the ion is more strongly hydrated also (according to their relative hydration enthalpies, $\Delta H_{Li}/\Delta H_{Cl} \sim 2$[31]). The LPEI/DCl system shows that the combined effect of using a charged polymer together with a weakly hydrated ion can cause a disturbance closer to the ion than was observed on previous occasions.

The extent to which $G_{Cl}(r)$ is perturbed is nevertheless remarkable in view of the fact that, at full neutralization, the charge density of LPEI is considerably lower than in a vinylic polymer such as PAA. Although further investigation is certainly called for, a possible explanation may be put forward tentatively: In LPEI the polyion charges are embedded in the backbone. At a high degree of ionization, screening of electrostatic interactions in the polycation may result in a closer distance of approach between polyion and counterion compared to systems in which the polyion charges are tethered on side chains. In fact, the location of charges within the LPEI backbone may hinder effective screening; in a quantitative analysis of the potentiometric behavior of LPEI,[32] the effect of non-fully-screened Coulombic interactions was suggested to be an important factor in determining the acidity of the polyion. At the point where half the monomers were charged ($\beta = {}^1/_2$), the acidity was shown to increase rapidly as a function of the charge density. This effect was also observed when salt was added. The physical explanation given to this effect is that at $\beta = {}^1/_2$, all next-nearest-neighboring N atoms are charged. Further protonation of the chain ($\beta > {}^1/_2$) becomes exceedingly difficult due to the inability of counterions to screen effectively the nearest-neighbor interactions within the polyion backbone.

NMR. The spin lattice relaxation rates R_1[20] of ^{35}Cl in an LPEI/HCl solution and in some low molecular weight salt solutions are shown as a function of concentration in Table 2 and Figure 5. It is observed that the LPEI has a considerable enhancing effect on the relaxation rate of Cl^-. A comparison of the rates at 1.5 m shows that LPEI has an effect on R_1 at least 10 times larger than low molecular weight (non-ion-paired) ionic solutions. This observation is consistent with a deformation of the Cl^- hydration sphere, as inferred from $G_{Cl}(r)$. Accordingly, it is concluded that a higher electric field gradient at the nucleus must at least be partly responsible for the relaxation rate

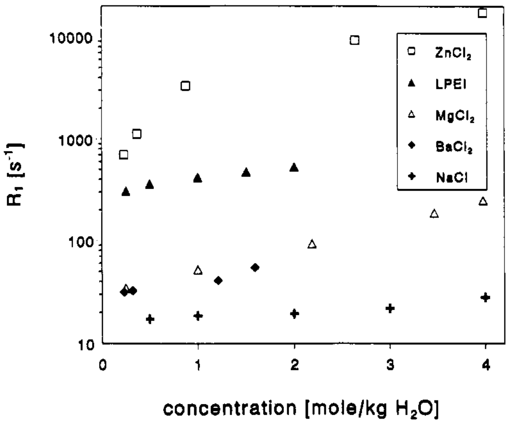

Figure 5. Relaxation rates (R_1) of $^{35}Cl^-$ as a function of concentration and counterion.

TABLE 2: Longitudinal Rates (R_1) of $^{35}Cl^-$ in Aqueous Solutions of LPEI/HCl, $ZnCl_2$, $BaCl_2$, $MgCl_2$, and NaCl

counterion	molality (mol/kg)	R_1 (s^{-1})	counterion	molality (mol/kg)	R_1 (s^{-1})
LPEI	0.25	306	Mg^{++} [35]	0.246	34.5
	0.50	360		0.99	51.9
	1.00	420		2.19	93.5
	1.50	476		3.47	189
	2.00	533		3.98	250
Zn^{++}	0.23	701	Na^+ [36]	0.50	17.3
	0.37	1120		1.00	18.6
	0.88	3330		2.00	19.4
	2.64	9320		3.00	21.9
	3.98	17400		4.00	28.0
Ba^{++}	0.23	31.5			
	0.32	32.5			
	1.21	40.7			
	1.59	54.7			

enhancement in LPEI/DCl solutions. It is interesting to note that in a $ZnCl_2$ solution,[24] where ion-pairing occurs, $G_{Cl}(r)$ is also markedly different from $G_{Cl}(r)$ in NaCl and that the features in $G_{Cl}(r)$ are strongly dependent on concentration. Since ion-pairing comes at a cost of symmetric hydration, Cl^- relaxation is expected to be extremely enhanced in these solutions, as can be observed in Figure 5. In fact, Cl^- relaxation is even faster in $ZnCl_2$ solution than in LPEI/DCl(aq).

In other concentrated polymer systems, the ion relaxation rate enhancement is less severe: e.g. in a 1.5 m PEO/NaCl (1:1) solution (Figure 4 in ref 33), the relative enhancement of Na^+ and Cl^- relaxation compared to the corresponding pure water values are 2 and 3, respectively. Similarly, in NaPAA at 1.09 m, the relative enhancement is 4.5.[34] In spite of the fact that the linear charge density, and the resulting electric field gradient from the polyion, is significantly higher in the vinylic polymer PAA than in LPEI, the latter invokes a far larger NMR effect. This may in part be explained by the greater perturbation of the primary hydration sphere.

Conclusions

The results of neutron diffraction isotopic substitution experiments and nuclear magnetic relaxation rate measurements on Cl^- in solutions of the polybase poly(ethylenimine) neutralized with hydrochloric acid are reported. The results are compared with those from solutions of low molecular weight chloride salts and other polyelectrolyte/polymer systems. It turns out that the spatial and orientational distribution of water in the first hydration shell of Cl^- is affected by the presence of the polycation. The nuclear magnetic relaxation of the Cl^- ions is strongly enhanced in the polyelectrolyte system. The neutron data indicate that this enhancement may at least be partly due to an increase in the electric field gradient at the Cl^- nucleus. The origin of this effect is to be sought in the asymmetric hydration of Cl^-, or possibly a direct Cl^-–polyelectrolyte interaction.

It is clear that further investigation in the small and intermediate *q* regime is necessary to elucidate the nature of the polymer–ion interaction. Comparing NDIS results from solutions containing isotopically dissimilar polymers is essential. A detailed knowledge of polyion–counterion interactions is of general interest for the understanding of many ion-induced effects observed in macromolecular systems. Examples of these effects are salting-out/salting-in (e.g. dextran) and conformational transitions in proteins and DNA. In view of the low-*q* effects observed, these interactions are relatively long range in the sense that they may be propagated through two (or more) solvent layers.

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