Polyelectrolyte effects on counterion self-diffusion

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Abstract. The self-diffusion coefficient of tetramethylammonium (TMA^+) counterion has been measured in aqueous solutions of polymethacrylic acid (PMA) of 100 and 1000 monomers as well as in persistence-length DNA fragment solutions. The concentration ranged from 5×10^{-4} M to 1 M (monomolar) and no low-molecular-weight salt was added. The counterion self-diffusion coefficient was found to be independent of the kind of polyion and of molecular weight over a large concentration range. In the low-concentration region the TMA^+ self-diffusion coefficient is a function of polyion length and species. In this concentration region the TMA^+ self-diffusion coefficient is the smallest in solutions of the polyion with the largest persistence length (TMADNA). The TMA^+ self-diffusion coefficients in solutions of the two PMAs start to deviate upon dilution at the crossover concentration from semidilute to dilute for the shorter PMA (100 monomers). In the dilute solutions of the short PMA (100 monomers) the counterion diffusion coefficient is lower than that in semidilute solutions of the higher-molecular-weight polyelectrolyte at the same monomer concentration.

1. Introduction

The self-diffusion coefficient of counterions in polyelectrolyte solutions is strongly influenced by the polyion [1–3]. This is mainly caused by the strong electrostatic interactions between the counterions and the chemically bonded charges on the polyion. In theories treating counterion self-diffusion in polyelectrolyte solutions the counterions move in the cylindrical electrostatic potential of an infinitely long polyelectrolyte [4–6]. The influence of the finite length of the polyion is disregarded in these theories. In this paper we report on the counterion self-diffusion in solutions of polyelectrolytes of different molecular weights over polyion concentrations ranging from 5×10^{-4} M to 1 M. The influence of the kind of polyion, the polyion length and the polyelectrolyte concentration on the self-diffusion of the counterion are discussed.

There are many references in the literature describing the diffusive motion of counterions in solutions of polyelectrolytes [7–17]. Counterion self-diffusion has been studied with different counterions [8, 14, 16, 17], in ordered solutions [7], as a function of ionic strength [9], of temperature [10, 11], of degree of neutralization [12, 17], and as a function of counterion charge [13, 15, 16]. Studies of the polymer concentration and molecular weight dependence of the counterion self-diffusion coefficient are not so abundant [18–20]. Ander and Lubas [19, 20] studied the Na^+ counterion diffusion as a function of polysaccharide concentration. They found a minimum in the counterion self-diffusion coefficient as a function of the polyelectrolyte concentration at 0.004 monomolar. Rymdén and Stilbs [18] observed a steep rise in the counterion self-diffusion coefficient below a polyion concentration of 0.01 molar for the tetramethylammonium (TMA^+) ion in polyacrylic acid

(PAA) solutions. The influence of the polyion molecular weight on the TMA$^+$ self-diffusion coefficient was not discussed. Theoretical predictions on the effects of the finite polyion length on thermodynamic quantities [21–25] indicate, however, that the effective counterion self-diffusion coefficient is a function of polyion length.

In this article we describe the experimental study of counterion self-diffusion in solutions of completely neutralized polymethacrylic acid (PMA) of approximately 100 and 1000 monomers over a large concentration range. Low-molecular-weight PMA was chosen to allow for the study of the counterion self-diffusion in the dilute polyion concentration regime. In this regime the polyions can substantially extend and will thus comply better with the rodlike model used in theories that treat polyion end effects. We also studied the counterion self-diffusion in solutions of TMADNA of 130 base pairs (about one persistence length). The persistence length of TMADNA hardly varies with polyion concentration, in contrast with the persistence length of a flexible polyelectrolyte like PMA [26]. To investigate possible end effects, the TMA$^+$ self-diffusion coefficient was measured in solutions of a methacrylic acid oligomer of about 15 monomers. The counterion dynamics in acetate solutions illustrate the difference between a solution of simple salt and a polyion solution.

The counterion self-diffusion coefficient was measured with pulsed field gradient (PFG) NMR. The TMA$^+$ counterion was chosen because of its high signal-to-noise ratio in the NMR spectrum due to the twelve identical protons and because of the favourable spin characteristics of the methyl groups. To test if TMA$^+$ could be used as a probe ion, we compared the counterion self-diffusion coefficients of the more commonly used Li$^+$ and Na$^+$ to that of TMA$^+$ in solutions of the PMA of 1000 monomers.

2. Theory

In theoretical descriptions of the diffusive motion of charged particles in polyelectrolyte solutions the polyion is usually considered to be of infinite length [4, 5, 6]. In the counterion condensation theory [4], the charge-density parameter, $\xi = \ell_b/b$, is introduced, where b is the contour distance between charges on the chain and ℓ_b is the Bjerrum length, $\ell_b = q^2/\epsilon kT$ (with q the protonic charge, ϵ the dielectric constant of the solvent, k the Boltzmann constant and T the absolute temperature). For values of ξ larger than one, counterions will condense on the polyelectrolyte chain. The polyion is considered as a charged line of infinite length in an infinitely diluted solution. The effective counterion self-diffusion coefficient D/D_0 calculated with the use of Manning's theory equals 0.29 for fully neutralized PMA. (D_0 is the self-diffusion coefficient of the counterion in infinitely diluted solutions of simple salt.) Yoshida [5] and Nilsson [6] introduced a polyion concentration dependence by making use of a cylindrical cell model [27]. The effective counterion diffusion coefficient at infinite dilution that is calculated with this model is, for completely neutralized PMA, equal to 0.49. The concentration dependence of the counterion self-diffusion coefficient in this model does not match experiment. Calculated values at low polyion concentrations ($c \lesssim 0.01$ monomolar) are too low; values at higher concentrations ($c \gtrsim 0.1$ monomolar) are too high.

Woodbury [23] derived end effect corrections to Manning's expression for the excess free energy. He showed that for chains of finite length L the excess free energy due to the polyion varies linearly with κL (for $\kappa L \ll 1$). From the partial derivatives of the excess free energy with respect to the number of particles and to the volume, respectively, the counterion activity coefficient γ_+ and the osmotic coefficient ϕ are calculated (in the case without added salt):

$$\ln \gamma_+ = \frac{-\gamma \xi n_p}{2\kappa^2}\left[1 + \frac{e^{-\kappa L} - 1}{\kappa L}\right] \tag{1}$$

$$\phi = 1 - \tfrac{1}{2}\xi\left[1 + \frac{\mathrm{e}^{-\kappa L} - 1}{\kappa L}\right] \tag{2}$$

where $\lambda = 4\pi q^2/\epsilon kT$ is the charging parameter and n_p is the number concentration of monomers (one charge per monomer). Both ϕ and γ_+ approach 1 at finite polyion concentrations. There is no expression for the counterion self-diffusion coefficient, but the concentration dependence of the diffusion coefficient was found [28, 29] to be in reasonable agreement with the concentration dependence of the osmotic and counterion activity coefficients.

3. Experimental details

The polymethacrylic acid (PMA) and the methacrylic acid oligomer used in this experiment were provided by Polymer Standard Services. The molecular weight distributions of the polymers and oligomer used were narrow ($M_w/M_n \leqslant 1.05$). The polymers contained 1000 monomers (PMA1000; average molecular weight, M_w, of the sodium salt: 112 500) and 100 monomers (PMA100; $M_w = 9800$, sodium salt), respectively. The oligomethacrylic acid (OMA10; $M_w = 1500$, sodium salt) consisted of approximately 15 monomers. The tetramethylammonium (TMA) acetate was of analytical grade. DNA fragments were obtained by a micrococcal nuclease digestion of calf thymus chromatin, following the procedure described before [30]. In order to narrow the molecular weight distribution, this material was further fractionated by means of gel permeation chromatography. The fraction used in the present experiments had a molecular weight of 0.86×10^5 g mol^{-1} (130 base pairs) of the sodium salt with $M_w/M_n = 1.1$, determined by gel permeation chromatography with light scattering detection. The sodium ions in the OMA10 salt and in the DNA sodium salt were exchanged with TMA$^+$ by means of a cation exchanging resin. The PMA sodium salts were acidified with an excess of hydrochloric acid and dialysed against freshly deionized water until the conductivity of the dialysis bath no longer decreased ($\leqslant 1 \times 10^{-6}$ Ω^{-1} cm^{-1}). The sodium content in all samples was determined by atomic absorption spectroscopy and was less than 0.1% of all counterions.

PMA1000 was neutralized to a neutralization degree of 0.8 by adding solutions of sodium, lithium and TMA hydroxide to solutions of PMA of known concentration. Concentration ranges of the solutions of Na$^+$ and LiPMA were made upon further dilution with water. The aqueous solution of TMAPMA was freeze dried and dissolved in D$_2$O. This was repeated until the NMR signals of the water and TMA$^+$ in the sample could be separated spectroscopically (volume percentage of water: $\leqslant 0.5$). Samples were prepared by diluting a stock solution of TMAPMA in D$_2$O to the desired concentrations.

Aqueous solutions of completely neutralized PMA100 and PMA1000 were prepared by titrating the polymer solutions with a solution of TMAOH. The TMAOH solution had been decarboxylated with an anionic exchanging resin in the hydroxide form. Solutions of TMAPMA, TMAOMA, TMAAc and TMADNA in D$_2$O were prepared over a broad concentration range as described above for the PMA1000.

Pulsed field gradient (PFG) self-diffusion measurements were done with the use of a Bruker AM 200 wide-bore magnet (4.7 T) linked to a Aspect 3000 (Bruker) unit. All measurements were done at 25 °C. The pulsed magnetic field was generated by an actively shielded gradient coil capable of generating a gradient up to 7.2 T m^{-1}. The calibration of the gradient was done by measuring the self-diffusion coefficient of pure water (2.30×10^{-9} m^2 s^{-1}) [31]. The filling height of the NMR tubes never exceeded 6 mm to ensure gradient homogeneity over the sample volume. Because of the large difference
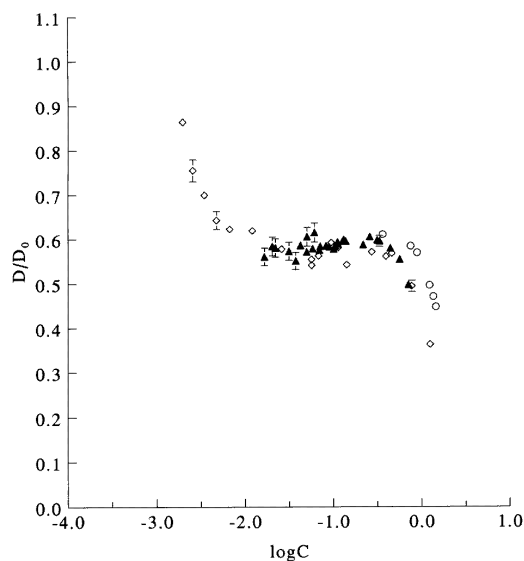
Figure 1. Experimentally (PFG NMR) determined values of the counterion diffusion coefficient as a function of polyion concentration in solutions of PMA1000; the degree of dissociation is 0.8; no added salt. Open diamonds: TMA^+; filled triangles: Li^+; open circles: Na^+.

between transversal and longitudinal relaxation rates of the nuclei of the counterions the stimulated pulsed-field-echo sequence [32] was used. The duration of the gradient pulse (δ) was 1 ms for the ^7Li nuclei, 2 ms for the ^1H nuclei and 3 ms for the ^{23}Na nuclei. After the gradient pulses there was a 0.2 ms delay before either applying the second radio-frequency pulse or before acquiring the signal. The time spacing (Δ) between two gradient pulses was 12 ms for the ^1H nuclei and 100 ms for the ^7Li and ^{23}Na nuclei. The echo attenuation is given by

$$A_G = A_0 \exp(-\gamma^2 G^2 \delta^2 (\Delta - \delta/3) D)$$

with A_0 the echo amplitude at zero magnetic field gradient, γ the gyromagnetic ratio of the nucleus, G the gradient amplitude and D the self-diffusion coefficient of the monitored nuclei. Typically about 30 different gradient values were used to measure the self-diffusion coefficient. These values were chosen in such a way that G^2 increased linearly. At the highest gradient value the echo attenuation was typically a factor e^{-4}.

4. Results and discussion

In figure 1 the effective self-diffusion coefficient of three counterions, Na^+, Li^+ and TMA^+, in solutions of PMA1000 at a degree of neutralization of 0.8 is plotted against the logarithm of the PMA monomolal (mol monomer kg^{-1}) concentration. It is clear from the graph that the diffusive behaviour of TMA^+ is similar to that of the sodium and lithium ions. The polymer concentration dependence of the counterion self-diffusion is the same for all three ions in the overlapping concentration range. The magnitudes of the self-diffusion coefficients of the counterions differ: the self-diffusion coefficient of Na^+ is larger than those of Li^+ and TMA^+. No pronounced minimum was found in the counterion self-diffusion coefficient as a function of polyion concentration.
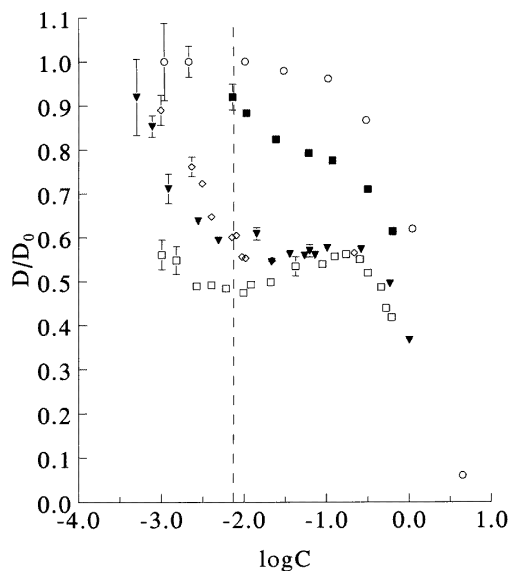
Figure 2. Experimentally (PFG NMR) determined values of the TMA$^+$ self-diffusion coefficient in solutions of persistence-length TMADNA (open squares), PMA1000 (open diamonds), PMA100 (filled upside-down triangles), PMA10 (filled squares) and acetate solutions (open circles); the degree of dissociation is 1.0; no added salt. The dashed line marks the concentration of the crossover between the dilute and semidilute concentration regimes for PMA100

At polymer concentrations from approximately 0.3 molal to 1 molal the effective counterion self-diffusion coefficient decreases from a value of about 0.6 to 0.4. At lower polymer concentrations, ranging from 0.01 molal to 0.3 molal, the self-diffusion coefficients of the Li$^+$ and TMA$^+$ ions appear to be concentration independent. At concentrations below 0.01 molal only the TMA$^+$ self-diffusion coefficient could be measured. The counterion self-diffusion coefficient shows a strong concentration dependence. Diluting the polymer solution from 0.01 to 0.001 molal causes the effective counterion self-diffusion coefficient to rise from 0.6 to 0.9. Contrary to the predictions of Yoshida [5] and Manning [4] the effective counterion diffusion coefficient approaches 1 upon diluting the polyelectrolyte solution. This confirms earlier experiments by Rymdén and Stilbs [18].

Figure 2 shows the TMA$^+$ self-diffusion coefficient as a function of polyion concentration over a large concentration range in solutions of completely neutralized OMA10, PMA100, PMA1000 and TMADNA of 130 base pairs. All concentrations are expressed in monomolal (one unit charge per monomer). Also displayed are the diffusion data on TMA$^+$ in TMA acetate solutions. The effective TMA$^+$ self-diffusion coefficient in the TMA acetate increases upon dilution and reaches the limiting value of 1 at a concentration of 0.3 molal. At concentrations lower than 0.3 molal the self-diffusion coefficient is constant. The effective TMA$^+$ self-diffusion coefficient in the polyelectrolyte solutions is smaller than the self-diffusion coefficient in the acetate solutions over the entire concentration range. This can be ascribed to the difference in the screening of the electrostatic potential. The screening by the counterions of the potential around the polyion is much less effective than the screening of the (spherical) potential of the small acetate ion.

Three concentration regions can be identified in the plot of the effective TMA$^+$ self-diffusion coefficient against polyion concentration. In the highest-concentration regime

($c \gtrsim 0.3$ monomolal) the counterion self-diffusion coefficient decreases, in the intermediate-concentration region (0.01 monomolal $\lesssim c \lesssim 0.3$ monomolal) the counterion diffusion coefficient is almost independent of polyion concentration, and in the most diluted region ($c \lesssim 0.01$ monomolal) the counterion self-diffusion coefficient increases upon dilution. In the high- and intermediate-concentration regions the effective counterion self-diffusion coefficient in the solutions of PMA1000, PMA100 and TMADNA is almost independent of the polyion species. This is remarkable, because the charge density of DNA ($\xi = 4.2$) is higher than the charge density of PMA ($\xi = 2.9$). There is some evidence, however, that the charge density of PMA is not so low. Lifson and Katchalsky [33] already mentioned that the structural value of the charge distance along the chain must be reduced in order to bring calculated values of the osmotic coefficient into accord with experimentally determined values of the osmotic coefficients in solutions of vinylic polyions like PMA. The osmotic coefficients in DNA were in better agreement with these calculations [34]. From recent neutron scattering experiments on solutions of PSS [35], a similar vinylic polyion, a intercharge distance of 1.6 Å was calculated. It seems reasonable to assume that the low value of the osmotic coefficient points to a higher charge density for PMA. If the intercharge distance in vinylic polyions is indeed about 1.6 Å this would result in a charge density of 4.3 instead of the commonly used value of 2.9. The similarity between the counterion self-diffusion coefficients in the PMA and DNA solutions confirms this hypothesis.

In the high-concentration region the diffusion coefficients decrease. The effective counterion self-diffusion coefficient in the acetate solution is higher than that in the polymer solutions. The values of the effective self-diffusion coefficient in the OMA10 solutions lay between those in the polymer and acetate solutions over the entire concentration range. In all solutions the downward trend to zero effective diffusion coefficient upon concentrating is obvious. Apparently at high concentrations polyelectrolyte effects become less important for counterion diffusion. The effective TMA$^+$ self-diffusion coefficient in the OMA10 solutions relative to that in the PMA solutions can be explained in terms of the weaker electrostatic potential of this short oligoion. The screening of this oligoion potential is less effective than the screening of the coulombic potential of the acetate ion. This may explain why the self-diffusion coefficient in OMA10 solutions lies between that in the polyion and acetate solutions. In the intermediate-concentration region the counterion self-diffusion in the polyion solutions does not vary with polymer concentration. The effective self-diffusion coefficient remains constant at a value of approximately 0.5, while that in the acetate solution already approaches 1.

In the most diluted region the effective counterion self-diffusion coefficient in the solutions of PMA100 and PMA1000 rises upon dilution to the value for free diffusion. This confirms the results of Rymdén and Stilbs [18], although they did not measure at these low polymer concentrations ($<5 \times 10^{-4}$ M) and did not find effective counterion diffusion coefficients this high (~ 0.9). The self-diffusion coefficients of TMA$^+$ in PMA1000 and PMA100 both start to rise upon dilution at a polyion concentration of approximately 0.01 monomolar. All TMA$^+$ self-diffusion coefficients in the PMA100 solutions lay below those measured in the solutions of PMA1000. This polyion length dependence has not been reported earlier.

The concentration dependence of the counterion activity coefficient calculated with expression (1) is plotted in figure 3. The rise of the activity coefficient upon dilution starts at higher concentrations for the shorter polyions. This should also be true for the counterion self-diffusion coefficient [36]. The experimentally determined dependence on the polyion length of the TMA$^+$ self-diffusion coefficients in PMA solutions contradicts predictions based on Woodbury's theory [23].
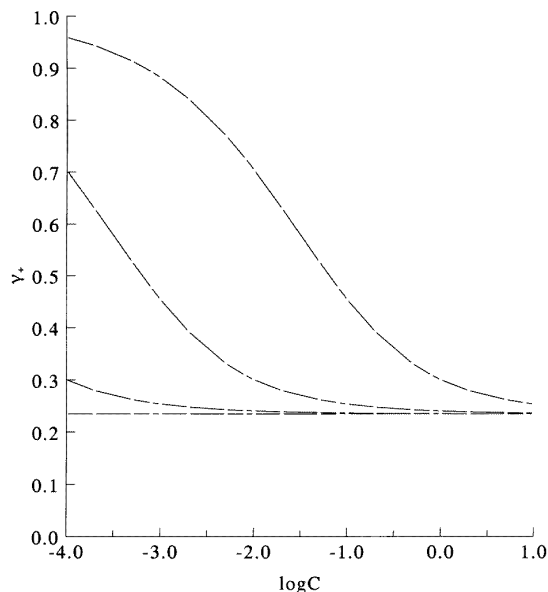
Figure 3. Calculated values (expression (1)) of the polyion concentration dependence of the counterion activity coefficient, γ_+, in solutions of polyions of varying contour length L, with a linear charge density $\xi = 2.9$. From top to bottom $L = 2.5$ nm, $L = 25$ nm, $L = 250$ nm, $L = $ infinite.

The effective self-diffusion coefficient of TMA$^+$ in the TMADNA solutions in this region is smaller than that in solutions of both PMA100 and PMA1000. The contour length of DNA, however, lies between that of PMA100 and PMA1000 ($L_{\text{PMA100}} \approx 20$ nm, $L_{\text{DNA}} \approx 40$ nm, $L_{\text{PMA1000}} \approx 200$ nm). Apparently, the polyion length is not the dominant factor in the rise of the counterion self-diffusion coefficient upon dilution. The TMA$^+$ self-diffusion coefficient is the smallest in the solutions of the polyion with the largest persistence length. The (concentration-dependent) persistence length of the methacrylic polyions has not been determined experimentally yet. According to theory [26], however, the electrostatic persistence length of flexible polyelectrolytes is larger for larger polyions. This means that the intermediate value of the counterion diffusion coefficient in the solutions of PMA100 between that in TMADNA and that in PMA1000 cannot be explained in terms of the electrostatic persistence length. It is remarkable that the TMA$^+$ self-diffusion coefficients in the solutions of PMA100 and PMA1000 start to deviate at the crossover concentration from the semidilute [37] to the dilute concentration regime for the shorter polymer. At these concentrations the short polyion can fully extend and can form a polyion lattice. The large polymer is still bent appreciably. Apparently, counterions can move more freely in the more disordered solution of the large polymer than in solutions of the short polyion.

5. Conclusions

The diffusive behaviour of the TMA$^+$ ion in polyion solutions is similar to that of the more commonly used counterions Li$^+$ and Na$^+$. The TMA$^+$ ion can be used as a probe ion in PFG NMR diffusion measurements. In this way the counterion self-diffusion coefficient can be measured in equilibrated systems down to concentrations of 5×10^{-4} M. The

TMA$^+$ self-diffusion coefficient is independent of polyion length in the semidilute and concentrated polyelectrolyte concentration regimes. The TMA$^+$ self-diffusion coefficient in solutions of TMADNA is equal to that in solutions of PMA over a large concentration range (from 0.01 monomolal to 1 monomolal). This points to a linear charge density of PMA close to that of DNA. This is in agreement with the low osmotic coefficient of PMA [33]. The concentration dependence of the TMA$^+$ self-diffusion coefficient at concentrations lower than 0.01 monomolal is a function of the stiffness of the polyion chain and of its length. In sufficiently diluted polyion solutions the effective TMA$^+$ self-diffusion coefficient approaches 1. The concentration dependence of the TMA$^+$ diffusion coefficient in polyion solutions cannot be explained with polyion end effect corrections to the counterion condensation theory alone.

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