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Counterion self-diffusion in polyelectrolyte solutions

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Abstract. The self-diffusion coefficient of Na^+ , Li^+ , tetra-methylammonium (TMA^+), tetra-ethylammonium (TEA^+), tetra-propylammonium (TPA^+) and tetra-butylammonium (TBA^+) in solutions of the weak polymethacrylic acid (PMA) were measured with PFG NMR. No additional salt was present in any of the experiments. The polyion concentration and degree of neutralization were varied. The maximum relative counterion self-diffusion coefficient against polyion concentration, that was reported earlier, was observed for both alkali and tetra-alkylammonium (TAA^+) counterions. We propose that the maximum is due to the combination of the obstruction by the polyion and the changing counterion distribution at increasing polyion concentration. An explanation of this proposal is offered in terms of the Poisson–Boltzmann–Smoluchowski (PBS) model for polyelectrolytes. Qualitative agreement of this model with experiment was found for the dependence of the counterion self-diffusion coefficient on the degree of neutralization of the polyion, on counterion radius and on polyion concentration, over a concentration range from 0.01 to 1 mol kg^{-1} . Adaption of the theoretical obstruction, to fit the self-diffusion data of the solvent, also greatly improves the model predictions on the counterion self-diffusion.

1. Introduction

In solutions containing polyelectrolytes the behaviour of the small ions, especially the counterions, is strongly influenced by the presence of the polyion. In comparison with the ions in simple salt solutions the counterions in polyelectrolyte solutions are appreciably disturbed, due to the strong interactions with the polyelectrolytes. The counterion self-diffusion coefficient in salt free polyelectrolyte solutions gives a good indication of the magnitude of these interactions [1, 2]. A general aspect of the counterion dynamics in polyelectrolyte solutions, the maximum of the counterion self-diffusion coefficient as a function of polyion concentration, has never been explained satisfactorily. This maximum has been reported for various counterions in solutions of natural and synthetic polyelectrolytes [3–5]. If the polyion is regarded as an infinitely long rod, it is possible to derive an expression for the counterion self-diffusion coefficient [6–8]. In the counterion condensation (CC) theory [8] the self-diffusion of a counterion in a salt free polyelectrolyte solution is determined by the charge density parameter ξ ($\xi = Q/b$, b is the distance between the charges on the polyion chain and Q is the Bjerrum length, $Q = e^2/(4\pi\epsilon\epsilon_0kT)$; with e the protonic charge, ϵ the relative dielectric constant of the solvent, ϵ_0 the dielectric constant of the vacuum, k the Boltzmann constant and T the absolute temperature). This theory is strictly valid at infinite dilution, and is therefore not useful to help explain the occurrence of the maximum of the counterion self-diffusion coefficient. The dependence on polyion concentration of the counterion self-diffusion coefficient is taken into account by the PBS model [6, 7]. This theory makes use of the cylindrical cell model for polyelectrolytes

[9, 10] and describes the self-diffusion of a point charge in the dielectric continuum around a cylindrical polyelectrolyte. A counterion radius can be introduced by adjustment of the distance of closest approach from the point charge to the polyion. In the theoretical section a short outline of this model will be given.

Here we report an investigation of the counterion self-diffusion in salt free polyelectrolyte solutions. We studied the dependence of the counterion self-diffusion coefficient on polyion concentration and degree of neutralization, as well as the influence of the radius and chemical characteristics of the counterions on the counterion self-diffusion. The dependence of the counterion self-diffusion coefficient on polyion concentration and counterion radius was studied with four tetra-alkylammonium (TAA^+) ions of increasing radius and two alkali ions, Na^+ and Li^+ . Self-diffusion measurements were made in PMA solutions at a fixed degree of neutralization over a large concentration range. The measured counterion self-diffusion coefficients were compared with those calculated with the PBS model. Ion specific effects were observed from comparison of the self-diffusion coefficients of the alkali and TAA^+ ions in PMA solutions. To study the influence of the charge of the polyion, the self-diffusion coefficient of TMA^+ in PMA solutions was measured at various degrees of neutralization, but at fixed polyion concentration. Results were compared with the predictions from the PBS model and, when possible, with CC theory. In addition, the solvent self-diffusion coefficient in the TMA–PMA samples was measured to estimate the counterion self-diffusion coefficient at zero electrostatic field and to investigate the role of the solvent in the self-diffusion of the counterions.

2. Experimental details

The polyelectrolyte used in this experiment was PMA, which was chosen because it is commercially available in very monodisperse samples. It was provided as the sodium salt by Polymer Standard Services. The weight average molecular weight (M_w) of the sodium PMA was 1.13×10^5 (approximately a thousand monomers; PMA1000). The molecular weight distribution of the polymer was narrow ($M_w/M_n \leq 1.05$; M_n is the number average molecular weight). An excess of hydrochloric acid was used to acidify the PMA sodium salt. Remaining salt and hydrochloric acid were removed by extensive dialysis (24 hours per run) with freshly deionized water. The dialysis was repeated until the conductivity of the external water was approximately equal to that of pure water ($\leq 1 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ at room temperature). One part of the resulting aqueous PMA solution was neutralized to degrees of neutralization (α), ranging from $\alpha = 0.1$ to $\alpha = 1$, with aqueous solutions of TMA hydroxide. The completely neutralized TMA–PMA sample was used in the solvent diffusion experiment. The remaining part of the PMA solution was divided into six portions and neutralized to a degree of neutralization of $\alpha = 0.8$ with aqueous solutions of sodium hydroxide (Merck Titrisol; 0.1 N), lithium hydroxide, TMA hydroxide, TEA hydroxide, TPA hydroxide and TBA hydroxide, respectively. An anionic exchange resin in the hydroxide form was used to prepare TEA, TPA and TBA hydroxide solutions from 0.1 N aqueous solutions of the halide salts (TEA and TBA bromide and TPA iodide). The resulting solutions were checked for the presence of halides with a solution of silver nitrate in phosphoric acid. No visible precipitation occurred. The TMA hydroxide used was a 10% aqueous solution of analytical grade. A lithium hydroxide solution was prepared from the solid hydroxide. Possible dissolved carbon dioxide was removed with an anionic exchange resin in the hydroxide form. The concentrations of the aqueous hydroxides and PMA solutions were determined potentiometrically. The titration curves of the titration of the hydroxide solutions with hydrochloric acid (Merck Titrisol; 0.1 N) showed only one point

of equivalence, indicating that no carbon dioxide was present in the solutions.

Because of the small difference in chemical shift in the NMR spectrum between the protons in water and in TAA⁺ ions D₂O was chosen as the solvent in the TAA–PMA solutions. To remove the water the aqueous TAA–PMA solutions were freeze dried and dissolved in D₂O. The solutions in D₂O were freeze dried again to further reduce the water content. This procedure was repeated until the NMR signals of the protons in TAA⁺ ions and water could be separated spectroscopically (amount of water ≤ 0.5%). Sodium and lithium PMA were kept in aqueous solutions. Samples over a large concentration range were made by dilution of the six PMA solutions, neutralized to a degree of $\alpha = 0.8$, and of the TMA–PMA solution at a neutralization degree of $\alpha = 1$. The TMA–PMA samples at various degrees of neutralization were diluted with D₂O to a polyion concentration of $c_p = 0.2 \text{ mol kg}^{-1}$ (mol monomer kg^{-1}).

Self-diffusion measurements were made with the pulsed field gradient (PFG) NMR method [11]. Use was made of a Bruker AM200 wide-bore magnet at a field strength of 4.7 T. The temperature in all experiments was kept constant at 25 °C. For the measurement of the self-diffusion coefficient of the TAA⁺ ions an actively shielded gradient coil was used, that could generate a gradient (G) up to $0.36 \text{ T m}^{-1} \text{ A}^{-1}$ at a current of 20 A. This gradient coil was manufactured by Professor Callaghan and co-workers at Massey University in Palmerston North, New Zealand. The gradient was calibrated by measuring the self-diffusion coefficient of pure water [12]. Because the transversal relaxation rates of the alkylammonium protons were larger than the longitudinal relaxation rates, the pulsed field stimulated echo method [13] was used. To measure the self-diffusion coefficient of D₂O and of the sodium and lithium ions a commercially built gradient coil from Doty Scientific Inc. was used. At a current of 20 A this gradient coil generated a gradient with an amplitude of $0.4 \text{ T m}^{-1} \text{ A}^{-1}$. Longitudinal and transversal relaxation rates of the ²D, ⁷Li and ²³Na nuclei were approximately equal, thus the conventional pulsed field gradient method was used. For the calibration of this gradient the self-diffusion coefficients of aqueous sodium and lithium chloride solutions [14] were measured. To ensure gradient homogeneity over the entire sample volume the filling height of the NMR tubes never exceeded 6 mm. The duration of the gradient pulse (δ) was 1 ms for the lithium ions, 2 ms for the alkylammonium ions and D₂O and 3 ms for the sodium ions. The time duration (Δ) between two gradient pulses was in the order of 10 ms for the alkylammonium and sodium ions, 20 ms for D₂O and 100 ms for the lithium ions. After each gradient pulse there was a delay of 0.2 ms for the relaxation of possible eddy currents. The self-diffusion coefficient can be determined from the decay of the spin echo at increasing magnetic field gradient:

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

with A_G the echo amplitude, A_0 the echo amplitude at zero magnetic field, γ the gyromagnetic ratio of the counterion and D the self-diffusion coefficient of the counterion. The magnetic field gradient values were chosen so that G^2 varied linearly and that the echo attenuation at the maximum gradient was of the order e^4 .

The TMA⁺ self-diffusion coefficient at infinite dilution, D_0 , was determined experimentally by measuring the TMA⁺ self-diffusion coefficient in solutions of TMAAc in D₂O over a large concentration range. At concentrations lower than 0.01 mol kg^{-1} TMAAc the self-diffusion coefficient no longer decreased. The value of the self-diffusion coefficient at this concentration was set at D_0 . D_0 of the ions TEA⁺, TPA⁺ and TBA⁺ were taken as the values of the self-diffusion coefficients of these ions in solutions of TEABr, TPAI and TBABr in D₂O at a concentration of 0.01 mol kg^{-1} . These values agreed very well with the literature [15].

3. The PBS model

The polyelectrolyte solution is divided into cylindrical cells. Each cell, with radius R , contains one polyelectrolyte, with radius a , stretched along the axis of the cylinder, and n counterions, regarded as point charges of valence $+z$. In our case $z = 1$ and the concentration of additional salt is zero. In the model the polyelectrolyte radius represented the geometric polymer radius plus the radius of the counterion, i.e. the distance of closest approach (DCA) for a counterion, pictured as a point charge. By adjustment of this distance the influence of a counterion radius is introduced. The counterions are distributed in the cell in a cylindrical Poisson–Boltzmann (PB) potential.

$$-(1/r)(d/dr)(r d\phi(r)/dr) = 4\pi Qn(R) \exp(-\phi(r)). \quad (1)$$

Here $\phi(r)$ is the reduced electrostatic potential, $\phi(r) = e\psi/(kT)$ and $n(R)$ is the number concentration of counterions at the outer border of the cylindrical cell. The reference point of the potential is chosen at the exterior cell border, $\phi(R) = 0$. Two boundary conditions have to be fulfilled. The first boundary condition follows from Gauss' theorem, $(d\phi(r)/dr)_{r=R} = 0$; the second follows from the condition of electro-neutrality of the cylindrical cell. Equation (1) can be solved analytically, in the absence of additional salt [10]:

$$\phi(r) = \ln\{2\pi Qn(R)r^2 \sinh[\beta \ln(Ar)]/\beta^2\}. \quad (2)$$

β and A are integration constants.

An expression for the counterion self-diffusion coefficient in the cylindrical cell is derived as follows [7]. The self-diffusion of the counterions in the cylindrical cell can be expressed as the sum of two contributions: self-diffusion along and perpendicular to the polyion chain. The counterion self-diffusion along the chain is assumed to be undisturbed:

$$D/D_0 \equiv D_r = \frac{1}{3} + \frac{2}{3}D_{\perp}/D_0. \quad (3)$$

D_0 is the self-diffusion coefficient of the counterion in an infinitely diluted solution of simple salt. From the condition of steady state for the local flux, \mathbf{j} , of the counterions,

$$\nabla \cdot \mathbf{j} = -D_0 \nabla \cdot (\nabla n + n \nabla \phi) = -D_0 (\nabla^2 n + \nabla n \cdot \nabla \phi + n \nabla^2 \phi) = 0 \quad (4)$$

the relative counterion self-diffusion coefficient is derived

$$D_r = \frac{1}{3} + \frac{2}{3}\pi b R^2 \chi(R)n(R) = \frac{1}{3} + \frac{2}{3}\chi(R)n(R)/\langle n \rangle \quad (5)$$

with $\langle n \rangle$ the average number concentration of counterions in the cylindrical cell and $\chi(R)$ is determined by the differential equation

$$d\chi/dr + \chi/r(\chi - rd\phi/dr) - 1/r = 0 \quad (6)$$

which describes the radial part of the divergence of the counterion flux, equation (4) (equation (6) is different from equation (22) in [7], because of a probably typographical error in that reference). Using equation (2), equation (6) was solved numerically, with a fourth- and fifth-order Runge–Kutta method, under the boundary condition $\chi(a) = 0$. The relative self-diffusion coefficient that was calculated using the solution of (6) was compared with the relative self-diffusion coefficient calculated from equation (24) of [6], which yielded the same result. For the calculations of the polyion concentration dependence of the counterion self-diffusion coefficient the following parameters were used: $b = 3.1 \text{ \AA}$ (a minimal intra-molecular charge distance of 2.5 \AA divided by the degree of neutralization, $\alpha = 0.8$); $a = 6, 7, 8$ or 9 \AA . The parameters that were used to calculate the dependence of the counterion self-diffusion coefficient on the polyion degree of neutralization were: $a = 6 \text{ \AA}$; minimal intra-molecular charge distance: 2.5 \AA and $c_p = 0.2 \text{ mol l}^{-1}$.

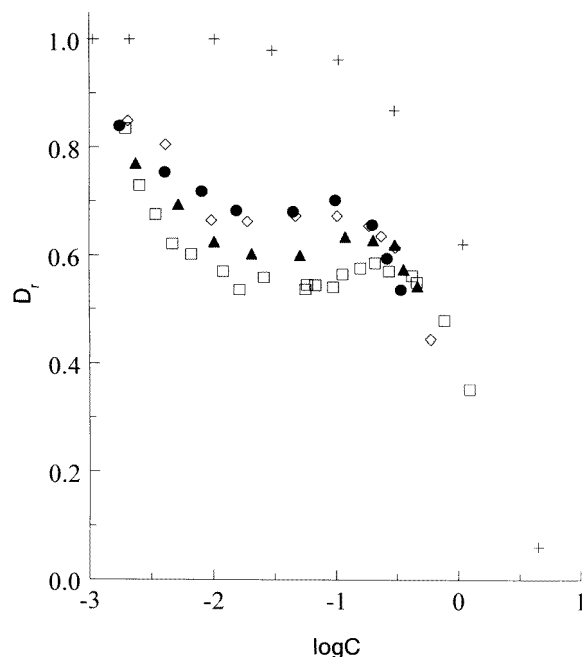


Figure 1. The relative self-diffusion coefficient of the TAA⁺ ions in salt free solutions of PMA in D₂O against the logarithm of polyion concentration. The PMA was neutralized to a degree of neutralization of 0.8. Open squares: TMA⁺, filled triangles: TEA⁺, open diamonds: TPA⁺, filled circles: TBA⁺, crosses: the relative self-diffusion coefficient of TMA⁺ in TMAAc solutions in D₂O.

4. Results and discussion

In figure 1 the relative self-diffusion coefficients of TMA⁺, TEA⁺, TPA⁺ and TBA⁺ in solutions of polymethacrylic acid in D₂O are plotted against the logarithm of polymer concentration. Data are collected in table 1. Also plotted on the graph is the relative self-diffusion coefficient of TMA⁺ in a solution of TMAAc in D₂O. In the acetate salt solution the relative TMA⁺ self-diffusion coefficient steadily increases upon dilution and reaches a limiting value at a concentration of about 0.01 mol kg⁻¹, that equals the literature value [15] of the TMA⁺ self-diffusion coefficient at infinitely diluted solutions of simple salt. The general concentration dependence of the self-diffusion coefficients of the tetra-alkylammonium ions in polymethacrylic acid solutions is entirely different. A distinction can be made between a low-, an intermediate- and a high-concentration region. In the intermediate-concentration region the counterion self-diffusion coefficient does not depend on polyion concentration. At high and low polyelectrolyte concentrations the counterion diffusion coefficient decreases with increasing concentration.

A maximum self-diffusion coefficient occurs for all tetra-alkylammonium ions (except TPA⁺) at $c_p \approx 0.1$ mol kg⁻¹. The maximum is found at higher polyion concentrations for smaller counterions. The value of the relative counterion self-diffusion coefficient, D_r^- , at the maximum increases with increasing counterion radius. In the intermediate-concentration region, down to a concentration of about 0.01 mol kg⁻¹, the counterion self-diffusion coefficient is concentration independent, but it does depend on the radius of the counterion. The value of the relative self-diffusion coefficient of the tetra-alkylammonium ions increases with increasing counterion radius in this concentration region.

Table 1. Relative self-diffusion coefficient (D_r) of TMA⁺ (mp8), TEA⁺ (ep8), TPA⁺ (pp8) and TBA⁺ (bp8) in solutions of PMA1000 in D₂O. The PMA1000 was neutralized to a degree of neutralization of 0.8. No simple salt was added to the solutions.

Concentration (mol kg ⁻¹)	D_r	Standard deviation
mp8		
1.244	0.35	0.005
0.771	0.48	0.005
0.459	0.55	0.005
0.420	0.56	0.004
0.272	0.57	0.004
0.209	0.59	0.005
0.158	0.58	0.005
0.113	0.56	0.008
0.094	0.54	0.01
0.068	0.54	0.01
0.058	0.54	0.01
0.056	0.54	0.01
0.026	0.56	0.01
0.016	0.54	0.01
0.012	0.57	0.01
0.0067	0.60	0.02
0.0047	0.62	0.02
0.0035	0.68	0.02
0.0025	0.73	0.02
0.0020	0.83	0.02
ep8		
0.465	0.54	0.02
0.358	0.57	0.02
0.303	0.62	0.02
0.202	0.63	0.02
0.119	0.63	0.02
0.051	0.60	0.02
0.021	0.60	0.02
0.010	0.63	0.02
0.0052	0.69	0.02
0.0024	0.77	0.02
pp8		
0.597	0.44	0.01
0.306	0.61	0.02
0.235	0.64	0.01
0.187	0.65	0.01
0.102	0.67	0.01
0.047	0.67	0.01
0.019	0.66	0.01
0.010	0.66	0.01
0.0041	0.80	0.01
0.0020	0.85	0.01
bp8		
0.341	0.54	0.004
0.262	0.59	0.004
0.198	0.66	0.004
0.098	0.70	0.01
0.045	0.68	0.01
0.015	0.68	0.01
0.008	0.72	0.01
0.0041	0.75	0.03
0.0017	0.84	0.02

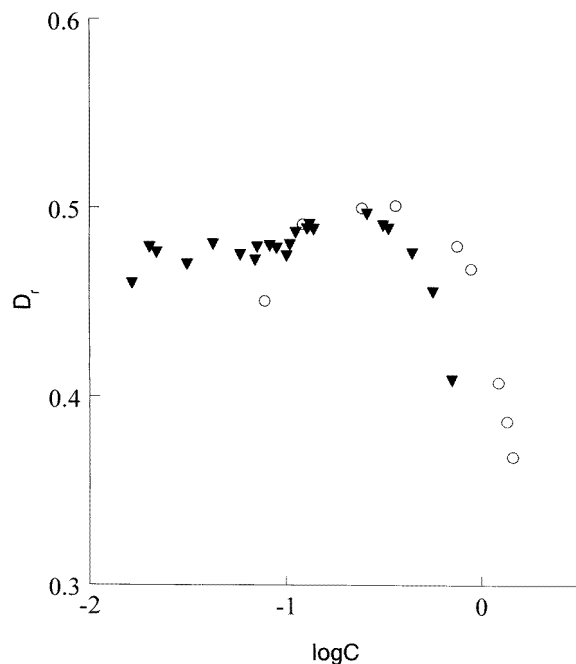


Figure 2. The relative self-diffusion coefficient of Na⁺ and Li⁺ in aqueous salt free solutions of PMA against the logarithm of polyion concentration. The PMA was neutralized to a degree of neutralization of 0.8. Open circles: Na⁺, filled upside-down triangles: Li⁺.

From $c_p \approx 0.1 \text{ mol kg}^{-1}$ for the TBA⁺ and the TPA⁺ counterions and $c_p \approx 0.2 \text{ mol kg}^{-1}$ for the TEA⁺ and the TMA⁺ counterions to higher polyion concentrations, the relative self-diffusion coefficient of all tetra-alkylammonium ions starts to decrease. The slope of the decrease in relative counterion self-diffusion coefficient against concentration was determined with a linear least-squares method for each counterion. The decay of the counterion self-diffusion coefficient is faster for larger counterions in the high-concentration region. The slope increases from a value of $-dD_r/dc = 0.25 \text{ kg mol}^{-1}$ for the TMA⁺ ion to a value of $-dD_r/dc = 0.84 \text{ kg mol}^{-1}$ for the TBA⁺ ion. This behaviour was expected on basis of the smaller available free volume for the larger ions. The volume fraction of polyelectrolyte, however, is still small at these concentrations ($\sim 10\%$, or $c_p \sim 1 \text{ mol kg}^{-1}$). The faster decay of the counterion self-diffusion coefficient for the larger counterions results in an inversion of the dependence of the relative counterion self-diffusion coefficient on counterion radius in this concentration region: in the high-concentration region the relative counterion self-diffusion coefficient decreases with increasing counterion radius.

In the low-concentration region (below $c_p \approx 0.01 \text{ mol kg}^{-1}$) the relative counterion self-diffusion coefficient of the tetra-alkylammonium ions starts to increase upon dilution of the polyelectrolyte solution. This, like the maxima, also seems to be a general aspect of counterion self-diffusion in polyelectrolyte solutions [16, 17]. As can be seen from the graph, the value of the relative self-diffusion coefficient of the TAA⁺ ions does not depend on counterion size at the lowest polyion concentrations. At $c_p \approx 0.002 \text{ mol kg}^{-1}$ the relative self-diffusion coefficient of all TAA⁺ ions, except TEA⁺, is approximately 0.85. D_r of TEA⁺ approaches this value. This behaviour is intuitively correct: at low concentrations the relative self-diffusion coefficient should not vary with particle size. It is remarkable,

Table 2. Relative self-diffusion coefficient (D_r) of Na^+ (np8) and Li^+ (lp8) in aqueous solutions of PMA1000. The PMA1000 was neutralized to a degree of neutralization of 0.8. No simple salt was added to the solutions.

Concentration (mol kg ⁻¹)	D_r	Standard deviation
np8		
1.443	0.37	0.01
1.350	0.39	0.01
1.225	0.41	0.01
0.883	0.47	0.01
0.748	0.48	0.01
0.362	0.50	0.01
0.243	0.50	0.01
0.121	0.49	0.01
0.078	0.45	0.02
lp8		
0.707	0.41	0.004
0.563	0.45	0.004
0.442	0.48	0.004
0.333	0.49	0.01
0.313	0.49	0.004
0.258	0.49	0.004
0.217	0.48	0.006
0.138	0.49	0.006
0.128	0.49	0.006
0.131	0.49	0.01
0.111	0.49	0.01
0.104	0.48	0.01
0.101	0.47	0.01
0.089	0.48	0.01
0.082	0.48	0.01
0.071	0.48	0.01
0.069	0.47	0.01
0.058	0.47	0.01
0.042	0.48	0.01
0.031	0.47	0.02
0.022	0.48	0.02
0.020	0.48	0.02
0.016	0.46	0.02

however, that the presence of the polyion, in the still semidilute polyelectrolyte solutions, hardly disturbs the diffusive motion of the counterions at these concentrations.

The self-diffusion coefficient of two alkali ions in aqueous solutions of PMA has been measured with PFG NMR. In figure 2 the relative self-diffusion coefficients of Na^+ and Li^+ against the logarithm of PMA concentration are displayed. Data are collected in table 2. Because of the lower signal to noise ratio of alkali ions compared to that of tetra-alkylammonium ions, it was not possible to measure the self-diffusion coefficient of Li^+ at concentrations lower than 0.01 mol kg⁻¹ and of Na^+ below 0.08 mol kg⁻¹. The concentration dependence of the relative counterion self-diffusion coefficient of alkali and tetra-alkylammonium ions is similar, although there are some differences. The self-diffusion coefficient of Li^+ remains constant over a polyion concentration ranging from 0.01 to 0.1 mol kg⁻¹. This was also observed for the self-diffusion coefficient of the

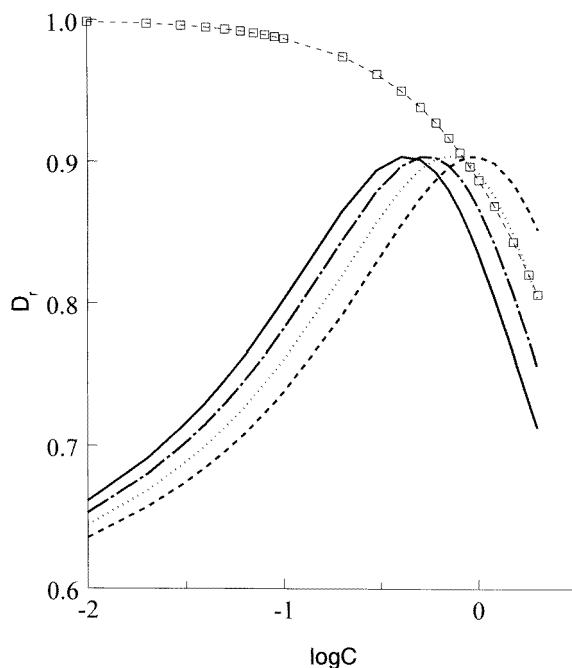


Figure 3. The theoretical relative self-diffusion coefficient (equation (5)) for four different distances of closest approach (DCAs) from a point charge to the polyion against the logarithm of polyion concentration. Dashed: DCA = 6 Å, $b = 3.1$ Å, dots: DCA = 7 Å, $b = 3.1$ Å, dashed-dot: DCA = 8 Å, $b = 3.1$ Å, full: DCA = 9 Å, $b = 3.1$ Å, dashed–open squares: DCA = 6 Å, $\phi = 0$.

tetra-alkylammonium ions. The value of the relative self-diffusion coefficient of the Li^+ counterion ($D_r \approx 0.5$) is approximately equal to that of the smaller TMA^+ ion. The self-diffusion coefficient of Na^+ could not be measured in this concentration region. The value of the relative self-diffusion coefficient of the alkali ions is approximately 10% lower than the relative self-diffusion coefficient of TAA^+ ions of the same size over the entire concentration range. This must be ascribed to the different chemical characteristics, or ion specificities, of the alkali and TAA^+ ions. Making a distinction in diffusive behaviour between ions solely on the basis of their radii [18–20] is only possible between like ions. The relative self-diffusion coefficient of Li^+ and Na^+ has a maximum as a function of polyion concentration. The maximum is found at $c_p = 0.25 \text{ mol kg}^{-1}$ for the Li^+ ion and at $c_p = 0.3 \text{ mol kg}^{-1}$ for the Na^+ ion. This is in accordance with the results of the TAA^+ ions, if it is considered that the hydrated Na^+ ion normally behaves as a smaller dynamic entity than Li^+ . In contrast to the TAA^+ ions the value of the self-diffusion coefficient of the alkali ions at the maximum does not depend on counterion radius. At polyion concentrations lower than that at the maximum, the relative self-diffusion coefficient of the smaller Na^+ ion lies below that of the Li^+ ion. This dependence on counterion radius was also found for the tetra-alkylammonium ions. The decay of the counterion self-diffusion coefficient in the high-concentration region has a faster rate for the larger counterion and the dependence of the relative counterion self-diffusion coefficient on counterion radius is inverted, as was also observed for the TAA^+ ions.

In figure 3 the relative counterion self-diffusion coefficients for four distances of closest approach, calculated from the PBS model, are plotted against the logarithm of polyion

concentration. The distances of closest approach are representative for the sum of the radius of the polyion (~ 2.5 Å) and the radii of the TAA⁺ ions, estimated on the basis of a radius of 3.5 Å for TMA⁺, which was calculated from neutron scattering experiments [18]. In comparing experimental data with the PBS model it must be realized that a real polyelectrolyte does not possess cylindrical symmetry over length scales larger than the persistence length. For flexible polyelectrolytes, like PMA, the persistence length [21–23] scales as κ^{-1} in the semidilute regime [24] ($\kappa = (4\pi Qn)^{1/2}$ is the Debye-Hückel screening parameter). The ratio of the persistence length and the radius of the cylindrical cell is of the order unity over the entire concentration range discussed here. Therefore, the assumption of cylindrical symmetry seems reasonable.

There is qualitative agreement with experiment over a polyion concentration range from 0.01 to 1 mol kg⁻¹. The calculated self-diffusion coefficients have a maximum as a function of polyion concentration, that shifts to higher polyion concentrations for the smaller ions. The value of the relative self-diffusion coefficient at the maximum does not depend on counterion radius as was also found for the alkali ions. At intermediate concentrations the relative self-diffusion coefficient increases with increasing counterion radius. In the high-concentration region the calculated slope is steeper for the larger ions, resulting in an inversion of the dependence of the relative counterion self-diffusion coefficient on counterion radius, as was also observed experimentally.

The maximum relative self-diffusion coefficient against polyion concentration, calculated with the PBS model, is explained as follows. According to the cell model, the electrostatic potential difference over the cell radius, $\Delta\phi$, falls off with decreasing cell dimensions, i.e. increasing polyelectrolyte concentrations. This causes an increase of the number of counterions at the outer cell boundary, where they can diffuse freely ($(d\phi/dr)_{r=R} = 0$), giving rise to a higher counterion self-diffusion coefficient upon concentration. However, at increasing polyion concentration the available free volume for the counterions diminishes, which results in a decrease of the counterion self-diffusion coefficient. This decrease, known as the obstruction effect, is calculated from the PBS model at $\phi = 0$. Equation (5) reduces to [7]

$$D_r = \frac{1}{3} + \frac{2}{3}(1 + a^2/R^2)^{-1}. \quad (7)$$

The obstruction effect, calculated for the TMA⁺ counterion ($DCA = 6$ Å), is plotted in figure 3 as well. Obviously the decrease of the relative self-diffusion coefficient at high polyion concentrations can be ascribed to obstruction. The combination of the obstruction effect and the increase of the number of counterions at the cell boundary upon concentration gives rise to the experimentally observed maximum of the relative counterion diffusion coefficient. If the obstruction effect is large, the maximum will appear at a lower polyion concentration.

The polyion concentration at the maximum and the steepness of the slope in the high-concentration region, calculated with equation (5), both differ by a factor of five with experiment. In addition, there is a difference between the experimental and theoretical value of the relative self-diffusion coefficient at the maximum ($D_r \sim 0.6$ and $D_r = 0.9$, respectively). There are some assumptions in the PBS model, which may be responsible for the quantitative disagreement between theory and experiment, over a polyion concentration range from 0.01 mol kg⁻¹ to higher concentrations.

First of all, the interactions between counterions are not taken into account. From the concentration dependence of the TMA⁺ self-diffusion coefficient in TMAAc solutions (figure 1) it is seen that these interactions become important at concentrations as low as 0.01 mol kg⁻¹.

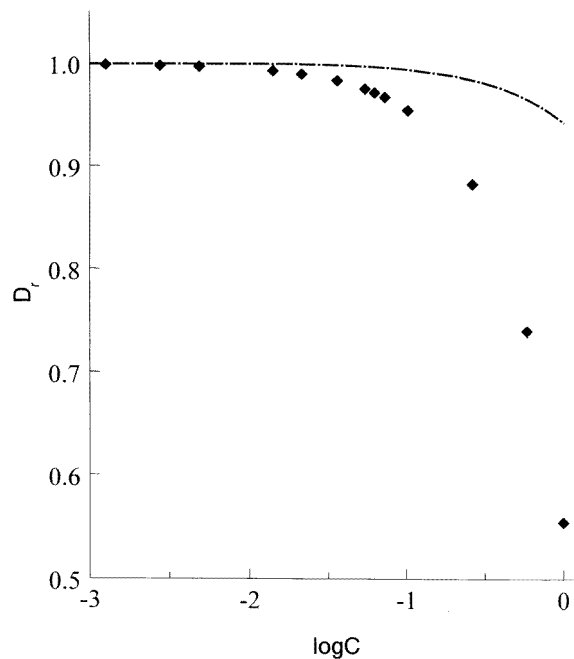


Figure 4. The relative self-diffusion coefficient of D₂O in salt free solutions of completely neutralized PMA against the logarithm of polyion concentration, with the theoretical relative self-diffusion coefficient of a particle in an uncharged polyelectrolyte solution. Filled diamonds: D₂O, dashed-dots: DCA = 4 Å, $\phi = 0$ (equation (7)).

Table 3. Relative self-diffusion (D_r) of the solvent (D₂O) in solutions of completely neutralized TMA–PMA1000. No simple salt was added to the solutions.

[pma] (mol kg ⁻¹)	D_r	Standard deviation
0.001	1.00	0.005
0.003	1.00	0.027
0.005	1.00	0.016
0.014	0.99	0.006
0.021	0.99	0.004
0.036	0.98	0.004
0.054	0.97	0.004
0.062	0.97	0.005
0.072	0.97	0.001
0.101	0.95	0.001
0.262	0.88	0.003
0.583	0.74	0.001
1.000	0.55	0.001

Secondly, it is assumed that particle motions in equipotential surfaces are undisturbed, not only neglecting counterion interactions, but also possible changes of the solvent properties close to the polyion, where the counterion density is high at all concentrations. From equation (7) it is easily calculated that this assumption leads to a maximum obstruction

effect (i.e. at a polyion volume fraction of 1) of $D_r = \frac{2}{3}$. To investigate the solvent perturbation, we have measured the solvent self-diffusion in TMA–PMA samples over a broad concentration range. The PMA used in this experiment was completely neutralized, to prevent deuterium exchange between the solvent and carboxylic acid groups on the polyion, for this would lower the observed solvent self-diffusion coefficient, especially at higher polyion concentrations. The results are plotted in figure 4, together with the calculated obstruction effect for D₂O (radius of D₂O ~ 1.5 Å). Data are collected in table 3. The self-diffusion coefficient of the solvent is reduced by up to 40% at a polyelectrolyte volume fraction of only approximately 10% (~ 1 mol kg⁻¹). Of course, the actual reduction of the solvent self-diffusion coefficient is only formally ascribed to obstruction by the polyion; it probably reflects a change of solvent properties near the polyion. Specific interactions, for instance the hydrogen bonding of polyions and solvent molecules, might diminish the solvent self-diffusion coefficient, especially at higher polyion concentration. These interactions would also add to the reduction of the counterion self-diffusion coefficient upon concentration, necessary for the observed maximum to occur.

If a value of the distance of closest approach is calculated by fitting equation (7) to the observed solvent self-diffusion coefficient, up to a polyelectrolyte volume fraction of only 1% ($c_p \approx 0.1$ mol kg⁻¹; at these concentrations specific interactions are probably not so important), a not very realistic polyion radius of 11 Å is found. Still, if this radius is used in equation (5), to calculate, for instance, the TMA⁺ counterion self-diffusion coefficient, the theoretical maximum and the slope in the high-concentration region coincide with experiment ($c_{max} \approx 0.2$ mol kg⁻¹, $-dD_r/dc \approx 0.3$).

A parameter in equation (5), which is sometimes adjusted to reconcile theory and experiment [25,26], is the distance between the charges on the chain, b . Taking the minimum intra-molecular charge distance to be 1.6 Å, however, only reduces the relative counterion self-diffusion coefficient at the maximum by 5% ($D_r = 0.9$, $b = 3.1$ Å compared to $D_r = 0.86$, $b = 2$ Å). An overestimation of the interchange distance of this magnitude does not seem to be an important reason for the quantitative differences between theory and experiment.

Summarizing, an apparent obstruction effect, that is much larger than predicted, and the interactions between the counterions lead to an experimental maximum of lower magnitude and at lower polyion concentrations than is calculated with the PBS model. The fact that a considerable increase of the polyion radius is needed to reconcile theory and experiment for both the ions and the solvent indicates that taking the solvent as an unperturbed continuum is a major flaw of the model.

In the low-concentration region there is qualitative disagreement between theory and experiment. At concentrations below the maximum the theoretical relative counterion self-diffusion coefficient decreases upon dilution, while the experimental relative self-diffusion coefficient starts to increase from a concentration of $c \approx 0.01$ mol kg⁻¹ to lower concentrations. In the model a finite fraction of counterions is found in the vicinity of the polyelectrolyte even at infinite dilution. Apparently, as the root mean squared distance of the counterions to the polyion increases, factors disregarded by PBS theory (for example: fluctuations, end effects and interactions with the solvent) become important and diminish the influence of the polyion on the counterions. If end effects were included in the PBS model, better agreement with experiment would result [27,28]. In a previous publication [29], however, we showed that the increase in counterion self-diffusion coefficient upon dilution could not be fully explained by taking into account the finite size of the polyion. The increase upon dilution rather was a function of the persistence length: the stiffer polyion maintained its influence on the counterions down to lower concentrations.

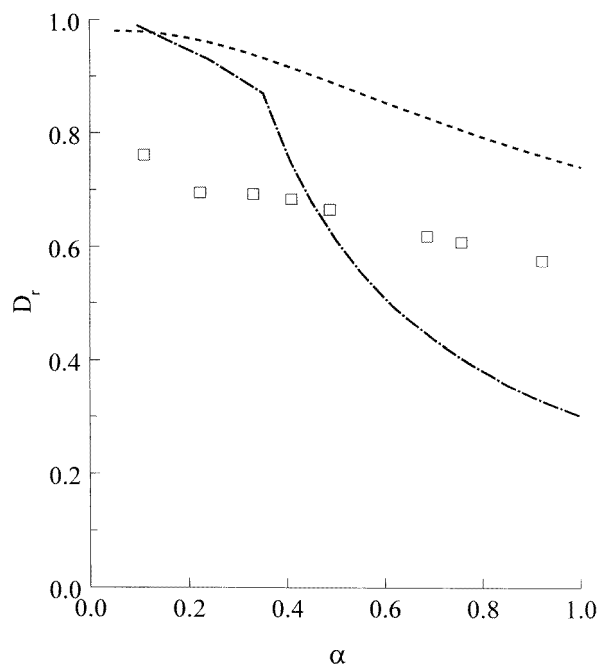


Figure 5. The relative TMA⁺ self-diffusion coefficient in solutions of PMA in D₂O against the degree of neutralization, at a PMA concentration of 0.2 mol kg⁻¹. The lines represent the relative counterion self-diffusion coefficients calculated from the PBS model (dashed, $c = 0.2 \text{ mol l}^{-1}$, $DCA = 6 \text{ \AA}$, $b = 2.5 \text{ \AA}/\alpha$) and with counterion condensation theory (dashed-dots, $\xi = 2.85\alpha$).

Table 4. Relative self-diffusion coefficient (D_r) of TMA⁺ in 0.2 mol kg⁻¹ solutions of PMA1000 in D₂O at different degrees of neutralization. No simple salt was added to the solutions.

α	D_r	Standard deviation
0.11	0.75	0.01
0.22	0.68	0.01
0.33	0.68	0.01
0.41	0.67	0.01
0.49	0.65	0.01
0.69	0.61	0.01
0.76	0.60	0.01
0.92	0.57	0.01

In figure 5 the relative self-diffusion coefficient of TMA⁺ in solutions of 0.2 mol kg⁻¹ PMA in D₂O is plotted against the degree of neutralization. The degree of neutralization ranges from $\alpha \approx 0.1$ to $\alpha \approx 1$. Data are collected in table 4. Also plotted in the graph are the relative counterion self-diffusion coefficients, calculated with the PBS model and with CC theory [8]. PMA is known to undergo a coil to globule transition upon neutralization at low α [30] ($\alpha \approx 0.2$). From our diffusion data this transition could not be observed. Since we only have two data points in this region, it will not be discussed here. Charging the polyion chain does not affect the counterion self-diffusion coefficient as strongly as

predicted by CC theory. At $\xi = 1$, or $\alpha = 0.35$, the observed counterion self-diffusion coefficient does not abruptly change, although there is evidence [31] that, even at these concentrations, a fraction of $(1 - \xi^{-1})$ of the counterions is associated with the polyion. CC theory underestimates the relative self-diffusion coefficient at low α , but overestimates it at higher α . The underestimation is probably due to the neglect of concentration effects, while the overestimation at $\alpha \geq 0.4$ probably arises because the assumption that condensed ions have zero mobility is too strong. The latter is in agreement with recent neutron scattering data on NaPSS [23], where, in order to explain the data, the fraction of free ions had to be chosen as 1, while osmotic measurements on solutions of vinylic polyions [25] could only be explained with a free fraction as low as 0.2.

With the PBS model the change at the inflection point (at $\alpha \approx 0.2$) is much weaker, which agrees better with experimental findings. The slope of the experimentally determined TMA⁺ self-diffusion coefficient against the degree of neutralization, $-dD_r/d\alpha$, is approximately 0.2, over the range from $\alpha = 0.2$ to $\alpha = 0.8$. The PBS result is slightly steeper, $-dD_r/d\alpha \approx 0.3$. Increase of the distance of closest approach results in a flattening of the slope, but agreement with experiment is already much better than with CC theory. The relative counterion self-diffusion coefficients, calculated with the PBS model, lay above the experimental values over the entire α -range. This agrees with the difference between the observed concentration dependence of the counterion self-diffusion coefficient and that calculated with the PBS model.

5. Conclusions

The self-diffusion coefficients of alkali and tetra-alkylammonium counterions show a similar dependence on polyion concentration. Both kinds of ion have a maximum relative self-diffusion coefficient as a function of polyion concentration. The maximum is predicted by the PBS model. According to this model, the maximum is caused by the combination of two opposing effects. At increasing polyion concentration, obstruction by the polyion leads to a smaller counterion self-diffusion coefficient. On the other hand, if the volume fraction of the polyions increases, the electrostatic potential difference over the cell radius decreases. This results in an increase of the number of counterions at the outer cell boundary, where the gradient of the electric field is zero and the ions can diffuse freely, giving rise to a higher counterion self-diffusion coefficient.

In the intermediate polyion concentration region the counterion self-diffusion coefficient does not depend on polyion concentration, but increases with counterion radius. The decay of the relative counterion self-diffusion coefficient at high polyion concentrations is faster for larger counterions, leading to an inversion of the dependence of the relative counterion self-diffusion coefficient on counterion radius. There is qualitative agreement between the predictions of the PBS model on the dependence of the counterion self-diffusion coefficient on polyion concentration in the concentration range from $c = 0.01$ to $c = 1$ mol kg⁻¹. The agreement is better for the alkali counterions. As is observed for the alkali ions, the value of the predicted relative self-diffusion coefficient at the maximum is independent of counterion radius. At polyion concentrations below 0.01 mol kg⁻¹ the relative counterion self-diffusion coefficient increases upon dilution, contrary to the predictions of the PBS model. Quantitative differences between experiment and PBS results become smaller, if the distance of closest approach to the polyion is increased, i.e. if the obstruction effect is chosen to be larger. This is also true for the dependence of the counterion self-diffusion coefficient on the polyion degree of neutralization. Adapting the obstruction effect, to accommodate the solvent diffusion data, also improves the theoretical predictions for the counterion diffusion.

The representation of the solvent seems to be an important difficulty with this model.

Charging the polyion does not affect the counterion self-diffusion coefficient very strongly. An inflection point, as predicted by both CC and PBS model, is not observed. The dependence on the degree of neutralization of the relative counterion self-diffusion coefficient as predicted by the PBS model is much better, despite the quantitative differences with experiment, than that of CC theory.

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