The influence of screening of the polyion electrostatic potential on the counterion dynamics in polyelectrolyte solutions

1998 J. Phys.: Condens. Matter 10 9207

(http://iopscience.iop.org/0953-8984/10/41/004)

J. Phys.: Condens. Matter **10** (1998) 9207–9220. Printed in the UK PII: S0953-8984(98)94860-3

The influence of screening of the polyion electrostatic potential on the counterion dynamics in polyelectrolyte solutions

F J M Schipper[†], J G Hollander and J C Leyte

Leiden Institute of Chemistry, Physical and Macromolecular Chemistry, Gorlaeus Laboratories, University of Leiden, PO Box 9502, NL-2300 RA, Leiden, The Netherlands

Received 5 June 1998, in final form 20 August 1998

Abstract. The self-diffusion coefficient of tetra-methylammonium counterion in solutions of polymethacrylic acid in D_2O has been measured over a broad polyion concentration range at a constant degree of neutralization and at different ratios of added monovalent or bivalent salt to polyions. A maximum counterion self-diffusion coefficient was observed as a function of polyion concentration. The value of the self-diffusion coefficient at the maximum did not depend on the valency of the added salt. The maximum was found at lower polymer concentrations and with a higher value, when the ratio of added salt to polyions was increased, as predicted by the Poisson–Boltzmann–Smoluchowski equation in the cylindrical cell model for polyelectrolytes. At higher polyion concentrations a maximum counterion self-diffusion coefficient against the ratio of added salt and polyions was observed, which has not been reported before. Upon increasing this ratio the electrostatic potential of the polyelectrolyte gets screened, leading to an increase of the counterion self-diffusion coefficient. Concentration effects of the added salt on the other hand ultimately lead to a decrease of the counterion self-diffusion coefficient, which explains the occurrence of a maximum.

1. Introduction

In a previous publication we investigated the dependence of the relative counterion self-diffusion coefficient, D_r, on polyion concentration, c_p, for four ions of increasing radii [1] in solutions without added salt. ($D_r = D/D_0$, D_0 is the solvent viscosity limited self-diffusion coefficient, D the actual self-diffusion coefficient of the counterions.) A maximum D_r against c_p was observed for all ions, but at different concentrations. Comparison of the experimental data with predictions from the Poisson–Boltzmann–Smoluchowski (PBS) cylindrical cell model [2, 3] showed good qualitative agreement at moderate and high c_p. A brief outline of the model is given here in the theoretical section. The maximum D_r could be explained with the use of the PBS model as follows. In a polyelectrolyte solution the motions of the counterions are influenced by the polyion in two ways.

First, there is a strong electrostatic interaction, due to the high charge of the polyelectrolyte. According to the model this interaction becomes smaller at higher polyelectrolyte concentrations. Due to the decrease of electrostatic potential difference over the cell radius the number of counterions at the outer cell boundary increases. Here, in the absence of the electric field of the polyion, they can diffuse freely. This effect will lead to an increase of D_r with increasing concentration.

[†] E-mail address: schipper@chemfcc.leidenuniv.nl.

0953-8984/98/419207+14$19.50

Second, counterion motions are hindered by the physical presence of the polyion. This so-called obstruction effect result will in a shorter diffusive path of counterions with increasing polyion concentration, leading to a decrease of D_r. The combination of these two effects will give rise to a maximum. The obstruction effect is larger for larger counterions, leading to a maximum at lower polyion concentrations when the counterion radius is increased, which was experimentally confirmed.

In this paper the effect of added salt on the electrostatic interaction between the polyion and the counterions, as judged by the position ($c_{p,max}$) and the value ($D_{r,max}$) of the maximum D_r, is discussed. If the explanation of the occurring maximum given is correct then screening of the polyion electrostatic potential, by addition of a normal electrolyte to the solution, must give rise, not only to an increase of D_r at the maximum, but also to a maximum at lower polyion concentrations than in polyion solutions without added salt. If the electrostatic disturbance of counterion motion by the polyion gets smaller, the concentration, where the effects of electrostatic interaction and obstruction on D_r match ($c_{p,max}$) must decrease as well.

In the present study the polymer concentration dependence of the relative self-diffusion coefficient of TMA^+ (tetra-methylammonium) was measured with pulsed field gradient (PFG) nuclear magnetic resonance (NMR) in heavy water polymethacrylic acid (PMA) solutions at different, but constant, ratios of polyelectrolytes and added salt. Experimental results were compared with relative counterion self-diffusion coefficients calculated with the PBS model. The experimental dependence of D_r of TMA^+ counterions on ionic strength in PMA solutions was also compared with predictions of the counterion condensation (CC) theory [4].

In order to study the influence of the valency of the added salt the TMA^+ self-diffusion coefficient was also measured in the presence of bivalent salt, again over a large polyion concentration range and at a constant fraction of counterions. The PMA was neutralized to a degree of neutralization, $\alpha = 0.8$. The mono- and bivalent salt under study were TMA chloride and magnesium chloride, respectively.

2. Experimental

The TMA^+ self-diffusion coefficients were determined with PFG NMR. The stimulated echo pulse sequence [5] was used because the transversal and longitudinal relaxation times of the ^1H nuclei in TMA^+ were unequal. Solutions were prepared in D_2O rather than in water, because of the small chemical shift between water and TMA^+ protons ($\sim$1.5 ppm). All measurements were done at a constant temperature of $25 \pm 0.1\,^\circ C$, which was controlled by a gas (pressurized air) thermostat. The height of the samples in the NMR tubes was always of the order 6–8 mm, to ensure that the magnetic field gradient was homogeneous over the sample volume. The magnet used was a Bruker AM200 wide bore magnet, operating at a magnetic field strength of 4.7 T, connected to a Bruker Aspect 3000 spectrometer. A magnetic field gradient, $G = 7.2$ T m^{-1} was generated at a maximum current of 20 A by an actively shielded gradient coil, constructed at Massey University, Palmerston North in New Zealand by the group of Professor P T Callaghan. The axis of the magnetic field gradient and the main magnetic field coincided. A Techron 7570 amplifier, coupled to the spectrometer, delivered almost rectangular gradients (from $G = 0$ to G_{max} and back within a constant time of approximately 100 μs) of duration $\delta \approx 2$ ms. The gradient was calibrated by measuring the self-diffusion coefficient of pure water [6] at $25\,^\circ C$ ($D_{water} = 2.30 \times 10^{-9}$ m^2 s^{-1}). Between two gradient pulses was a waiting period, $\Delta \approx 10$ ms. After each gradient pulse was a delay of at least 0.1 ms, to allow for the relaxation of possible eddy currents, prior to the application of the second radio frequency (rf) pulse or the signal accumulation. The amplitude of the Fourier transform of the acquired signal (not showing any significant deformation, suggestive of remnant gradients or pulse displacement) is given by

$$A_G = A_0 \times \exp\left[-\gamma^2 G^2 \delta^2 \left(\Delta - \frac{\delta}{3} \right) \times D \right]$$

with A_0 the echo amplitude at zero gradient, γ the gyromagnetic ratio and D the self-diffusion coefficient of the specific nucleus. D was determined experimentally by varying the magnitude of the magnetic field gradient.

PMA of approximately a thousand monomers ($M_W = 1.13 \times 10^5$) was provided as the sodium salt by Polymer Standard Service. The molecular weight distribution of the polyelectrolyte was narrow ($M_W/M_N < 1.05$, M_W, M_N are the weight and number-averaged molecular weights). A dilute solution of hydrochloric acid (Merck Titrisol; 0.1 N) was added in excess to an aqueous solution of the polyelectrolyte. Sodium chloride and the remaining hydrochloric acid were removed from the solution by repetitive dialysis against deionized water. Dialysis continued until the conductivity of the external solute, after equilibration, equalled that of pure water ($\Lambda \lesssim 1 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature). The acidic PMA solution was neutralized to $\alpha = 0.8$ with a TMA-hydroxide (TMAOH) solution of analytical grade (Merck; 10% aqueous solution). Before use, potential dissolved carbon dioxide had been removed from the TMAOH solution with an anionic exchange resin in hydroxide form. Potentiometric titration of the resulting TMAOH solution revealed one point of equivalence, indicative of the successful removal of possible carbon dioxide. Aqueous solutions of TMA–PMA at different ionic strength were made by addition of TMACl (Fluka) and $MgCl_2$ (Merck) solutions. Before using the TMA-chloride, it had been recrystallized from iso-propylalcohol, filtrated, flushed with ethanol and dried in a vacuum stove for 24 h. Finally, the TMA–PMA solutions were frozen, after which the solvent was evaporated under high vacuum. Then the dried TMA–PMA was dissolved in D_2O again and the previous procedure was repeated, until the water content in the samples was smaller than 0.5%. Samples over a broad concentration range were made by solution of the dry TMA–PMA in D_2O. The exact composition of the samples can be found in tables 1 and 2.

Additional samples at two polyion concentrations ($c_p \approx 0.017$ and $c_p \approx 0.15$ (mol monomer) (kg solution)$^{-1}$ were made by mixing samples of approximately the same polymer concentration, but of different ionic strength. In table 3 the concentrations and ionic strengths of the samples are displayed.

3. Theory

3.1. The PBS model

An expression for the self-diffusion of a counterion or coion (with a charge of opposite or equal sign to that of the polyion) in a solution containing polyelectrolytes can be derived by solving the Smoluchowski equation subject to the Poisson–Boltzmann (PB) potential in the cylindrical cell for polyelectrolytes. The cylindrical cell, radius R, contains one polyelectrolyte molecule of radius a, bearing n charges of charge $-e$, surrounded by counter- and coions (treated as point charges of charge $+z_i e$ or $-z_i e$) and immersed in a dielectric continuum. The PB equation in cylindrical coordinates can be expressed as

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\varphi(r)}{\mathrm{d}r} \right) = -\frac{e^2}{\varepsilon_0 \varepsilon_r kT} \sum_i n_i z_i \times \exp(-z_i \varphi(r)) \tag{1}$$

Table 1. Relative TMA$^+$ self-diffusion coefficient, D_r, in solutions of PMA at a degree of neutralization $\alpha = 0.8$. The ratio of counterions of the added salt and counterions of the polyion, $Y = [\text{TMA}^+]_{TMACl}/[\text{TMA}^+]_{TMAPMA}$, is constant over the concentration range.

c_p (mol kg^{-1})	D_r	Standard deviation
$Y \approx 0$; ([TMACl] = 0)		
0.016	0.54	0.01
0.058	0.54	0.01
0.068	0.54	0.01
0.113	0.564	0.008
0.158	0.581	0.005
0.209	0.585	0.005
0.272	0.571	0.004
0.394	0.558	0.005
0.771	0.477	0.005
$Y = 0.33$		
0.018	0.64	0.01
0.037	0.65	0.01
0.064	0.666	0.007
0.116	0.676	0.002
0.191	0.670	0.003
0.432	0.64	0.003
$Y = 0.67$		
0.017	0.71	0.01
0.035	0.72	0.01
0.076	0.727	0.003
0.100	0.723	0.003
0.166	0.713	0.002
0.372	0.639	0.004
$Y = 1.0$		
0.016	0.76	0.01
0.029	0.764	0.004
0.045	0.766	0.002
0.066	0.760	0.003
0.126	0.744	0.002
0.165	0.735	0.002
$Y = 10$		
0.017	0.912	0.002
0.030	0.884	0.002
0.044	0.866	0.002
0.092	0.779	0.002
0.145	0.683	0.004
0.220	0.625	0.004

where r is the position in the cylindrical cell, $\varphi = e\psi/kT$ is the reduced electrostatic potential, $\varepsilon_0\varepsilon_r$ the dielectric constant of the solvent, n_i the number concentration at zero potential and z_i the valence of small ion i, respectively, e is the elementary charge quantum, k the Boltzmann constant and T the absolute temperature. Equation (1) was solved numerically in the interval from a to R, under the boundary conditions $\varphi(R) = 0$ and $\varphi'(R) = 0$, for systems containing two and three species of small ions, respectively (n_1, n_2, n_3; z_1, z_2, z_3; $n_2 = 2n_3$, $z_1 = 1 = -z_2 = -0.5z_3$). The following parameters were used in

Table 2. Relative TMA$^+$ self-diffusion coefficient, D_r, in solutions of PMA at a degree of neutralization $\alpha = 0.8$. The charge normalized ratio of counterions of the added salt and counterions of the polyion is constant over the concentration range ($Y = 2 \times [\mathrm{Mg}^{2+}]/[\mathrm{TMA}^+]$).

c_p (mol kg^{-1})	D_r	Standard deviation
$Y = 0.21$		
0.017	0.68	0.01
0.031	0.69	0.01
0.085	0.69	0.01
0.102	0.704	0.003
0.120	0.713	0.005
0.167	0.707	0.002
$Y = 0.41$		
0.017	0.81	0.02
0.033	0.80	0.01
0.040	0.78	0.01
0.053	0.794	0.005
0.080	0.791	0.002
0.092	0.774	0.002
0.166	0.740	0.003
$Y = 0.61$		
0.017	0.86	0.01
0.500	0.84	0.01
0.090	0.83	0.01
0.164	0.802	0.002
0.191	0.774	0.002
0.314	0.725	0.001

Table 3. Relative TMA$^+$ self-diffusion, D_r, in PMA solutions at a degree of neutralization $\alpha = 0.8$, at different ratios of added salt to polyionic counterions, Y, for two polyion concentrations, $c_p \approx 0.017$ and $c_p \approx 0.15$ mol kg^{-1}.

Y	D_r ($c_p \approx 0.017$) (mol kg^{-1})	Standard deviation	D_r ($c_p \approx 0.15$) (mol kg^{-1})	Standard deviation
1.79	0.81	0.01		
2.43	0.82	0.02		
5.46	0.87	0.01		
7.07	0.897	0.005		
3.13			0.76	0.01
4.88			0.73	0.01
7.72			0.69	0.01

the calculation: distance of closest approach, $a = 6$ Å; the ratio of counterions of the added salt and of the polyelectrolyte, $Y = z_s n_s / z_c n_c$ (z_c, n_c, z_s, n_s, the valence and concentration of the counterions of the polyion and of the added salt) and the distance between charges on the chain, $b = l_m/\alpha = 3.13$ Å ($l_m = 2.5$ Å, the shortest distance between two adjacent monomers, $\alpha = 0.8$, the degree of neutralization of the polyion). The numerical solution is used to calculate the relative small ion self-diffusion coefficient [3] (here: monovalent counterions)

$$D_r = \frac{1}{3} + \frac{2}{3}\frac{\chi(R)}{\langle \exp(\varphi)\rangle} = \frac{1}{3} + \frac{2}{3}\frac{n(R)}{n_{avg}}\chi(R) \tag{2}$$

where the brackets denote the positional average of the exponent of the reduced electrostatic potential, n_{avg} is the number average concentration of counterions and $\chi(R)$, related to the counterion flux in the cylindrical cell, is determined by the first-order differential equation

$$\chi'(r) = \frac{1}{r} - \frac{\chi^2(r)}{r} + \varphi'(r) \tag{3}$$

which was solved using a fourth-order Runge–Kutta procedure.

3.2. The CC theory

Counterion condensation (CC) theory treats the polyion as a line charge of infinite length with a homogeneous charge distribution. The behaviour of the counter- and coions in the solution is described with the charge density parameter, $\xi = l_b/b$ ($l_b = z_p^2 e^2/(4\pi\varepsilon_0\varepsilon_r kT)$, the Bjerrum length; z_p is the valence of the charged monomer) and Y.

If the distance between the charges becomes smaller than the Bjerrum length counterions are assumed to condense on the chain. Uncondensed counterions and coions are treated with the Debye–Hückel approximation. In order to avoid problems concerning the identity of the condensing counterion, CC theory will only be discussed for monovalently charged polymers, monovalent counterions and 1–1 added salt. This way the validity of the Debye–Hückel approach is also not offended.

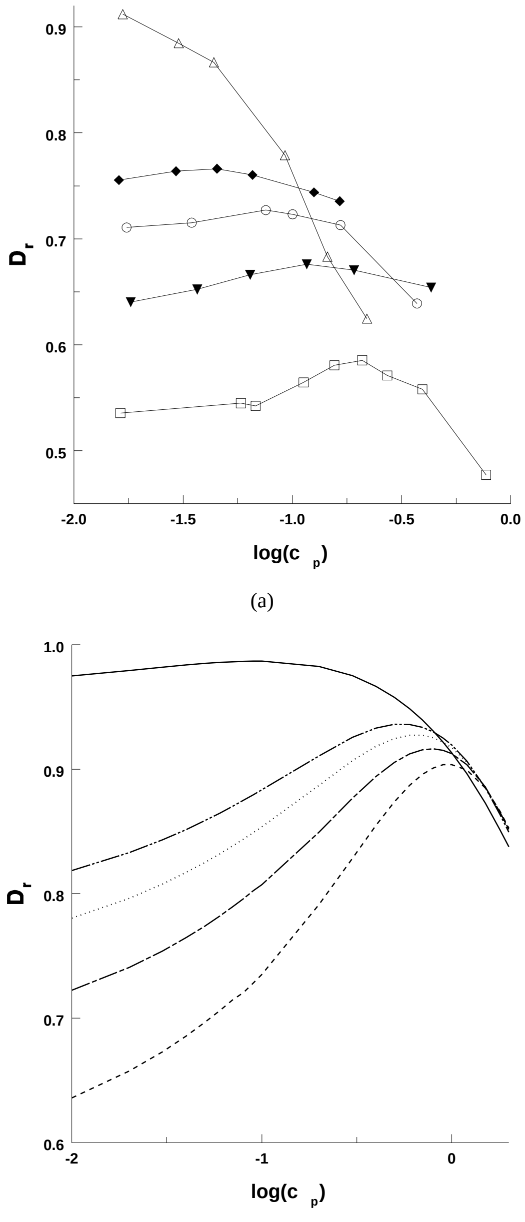
For univalent charges the condensation threshold value of the charge density parameter is $\xi = 1$. For values of $\xi > 1$ a fraction ξ^{-1} of the counterions condenses on the chain. If it is assumed that condensed counterions have zero mobility, the relative self-diffusion coefficient of the counterions can be expressed as [4]

$$D_r = Y(\xi^{-1} + 1)(1+Y)^{-1} \times \sum_{m_1=-\infty}^{\infty}\sum_{m_2=-\infty}^{\infty} [\pi(m_1^2 + m_2^2) + 1 + 2\xi^{-1}Y]^{-2} \tag{4}$$

$(m_1, m_2) \neq 0$, and integers; $\xi \geqslant 1$.

4. Results

Figure 1(a) depicts D_r of TMA$^+$ in heavy water solutions of PMA with added TMA chloride against the logarithm of polyion concentration (c_p in mol monomer kg^{-1} solution) at different ratios of added salt and counterions ($Y = 0$, 0.33, 0.67, 1, 10, respectively). Data are collected in table 1. As becomes clear from the graph a maximum D_r against polyion concentration appears at all but the highest concentration of added salt. The maximum is less pronounced, when the ionic strength increases and completely disappears at the highest salt concentration. With increasing ionic strength $c_{p,max}$ decreases, while $D_{r,max}$ increases with the concentration of excess salt. The maximum is caused by the combination of two opposing effects [1]. With increasing polyion concentration the electrostatic disturbance of the counterions by the polyion decreases, resulting in a rise of D_r. At the same time the increase in concentration causes a growing topological constraint on the counterion dynamics. Applying this to the experimental results it is easy to understand that $D_{r,max}$ is found at lower polyion concentrations, with values closer to one and finally vanishes completely, if the fraction of counterions decreases. Screening of the polyion by excess



(a)

(b)

Figure 1. (a) The relative TMA$^+$ self-diffusion coefficient, D_r, against the logarithm of PMA concentration, $\log(c_p)$, at a degree of neutralization, $\alpha = 0.8$, with added TMACl. The ratio of concentrations of the added salt and counterions of the polyions, Y, is constant over the concentration range. □, $Y \approx 0$; ▼, $Y = 0.33$; ○, $Y = 0.67$; ◆, $Y = 1.0$; △, $Y = 10$. The lines are drawn as guides to the eye. (b) The relative monovalent counterion self-diffusion coefficient, D_r, calculated with the PBS model against the logarithm of polyion concentration, $\log(c_p)$, with added monovalent 1–1 salt. The ratio of counterions of the added salt and counterions of the polyions, Y, is constant over the concentration range, distance of closest approach, $a = 6$ Å, distance between charges on the chain, $b = 3.13$ Å. Dashed curve, $Y = 0$; dashed-dotted curve, $Y = 0.33$; dotted curve, $Y = 0.67$; dashed-double dotted curve, $Y = 1$; full curve, $Y = 10$.

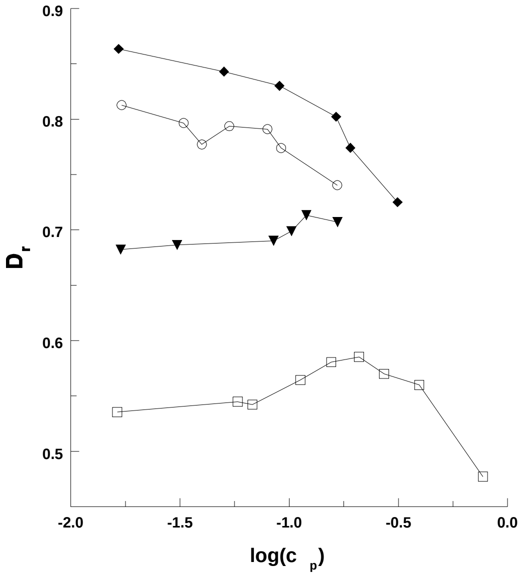
salt leads to a smaller electrostatic disturbance of the counterions and a higher relative counterion self-diffusion coefficient. So $D_{r,max}$ at the concentration where the obstruction effect and the effects of the electrostatic disturbance on counterion dynamics match, occurs at lower polyion concentrations, when the topological constraint is still small. In other words, at polyion concentrations below the maximum there is a concentration region where the counterion dynamics are governed by the electrostatic interactions of the counterions with the polyion, while at concentrations above the maximum the dynamics are dominated by the obstruction effect.

In fact, a third concentration region can be distinguished for the self-diffusion of counterions in polyelectrolyte solutions [1]. At polyion concentrations lower than reported here ($c_p < 0.01$ mol kg^{-1}), D_r increases upon dilution. Data in this concentration regime are not reported, because we were primarily interested in the behaviour of D_r around the maximum and next to this the error margins of the experimental data at concentrations below $c_p \approx 0.01$ mol kg^{-1} become of the order of the differences between the relative counterion diffusion coefficients at different Y. So, the intermediate concentration region, from $c_p \approx 0.01$ mol kg^{-1} to $c_{p,max}$, the concentration region where the counterion dynamics depend on the electrostatic interactions with the chain, gets smaller upon addition of salt and finally vanishes at the highest salt concentrations.

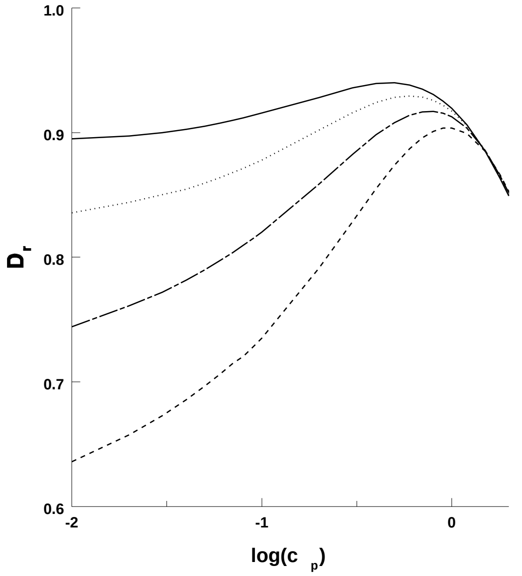
The theoretical dependence of D_r on polyion concentration at different ratios of polyelectrolytes and added salt (figure 1(b)) shows that there is good qualitative agreement between experiment and the PBS cylindrical cell model up to the highest amounts of added salt. A maximum relative counterion self-diffusion coefficient against polyion concentration is calculated, that shifts to lower polyion concentrations if the concentration of excess salt is increased and has almost disappeared at the highest ratio of excess salt to polyions. The maximum, however, is calculated at higher concentrations and with a higher value than experimentally observed. Quantitative disagreement is more pronounced in the absence of an added electrolyte. If Y increases from 0 to 10, the predicted counterion self-diffusion coefficient at the maximum increases from 0.90 to 0.94, while the experimental $D_{r,max}$ increases from $D_{r,max} = 0.59$ to $D_{r,max} = 0.77$ in this range. In experiment $c_{p,max}$ gets four times smaller with this increase in Y (from $c_{p,max} = 0.21$ to 0.05 mol kg^{-1}), while the theoretical $c_{p,max}$ decreases only twofold.

Figure 2(a) shows the concentration dependence of D_r of TMA$^+$ at different ratios of added Mg^{2+} and TMA$^+$ counterions in TMA–PMA solutions with added $MgCl_2$. Data are collected in table 2. In figure 2(b) the calculated values are plotted. Again, as was the case upon addition of monovalent salt, the maximum appears at lower polyion concentrations when the ratio of salt to polyions is increased. Comparison with calculated values shows that there is reasonable qualitative agreement for the TMA$^+$ relative self-diffusion coefficient over the two concentration ranges with the lowest ionic strength ($Y = 0.2$ and 0.4, respectively), but there are quantitative differences, as was observed for the monovalent ions. At the highest ratio of Mg^{2+} to TMA$^+$ ($Y = 0.6$) no maximum D_r was observed in experiment. The calculated curve still shows a distinct maximum.

The maximum has almost vanished when the concentration of Mg^{2+} is only approximately 20% that of TMA$^+$. The polyion concentration at the maximum ($c_{p,max} = 0.05$ mol kg^{-1}) upon addition of bivalent salt is equal to $c_{p,max}$ upon addition of five times as much monovalent salt. If the polyion concentration at the maximum is plotted against the charged normalized ratio of counterions of the added salt and polyionic counterions, Y (figure 3(a) ($Y = [\mathrm{TMA}^+]_{TMACl}/[\mathrm{TMA}^+]_{polyion}$ or $Y = 2 \times [\mathrm{Mg}^{2+}]/[\mathrm{TMA}^+]_{polyion}$), it is seen that bivalent counterions are much more efficient in balancing the electrostatic and obstruction effects on the counterion self-diffusion than the univalent counterions.

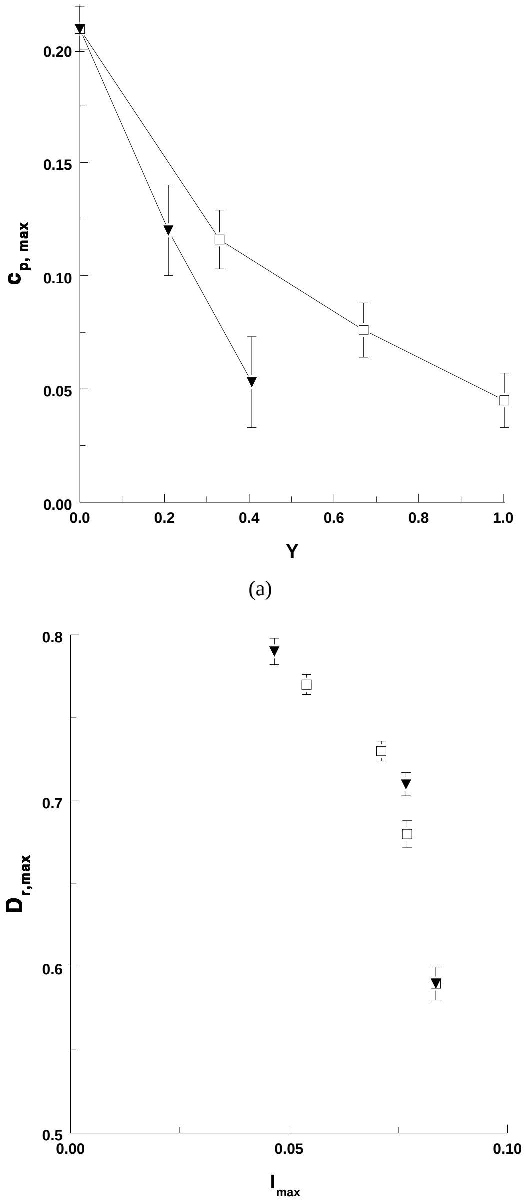


(a)



(b)

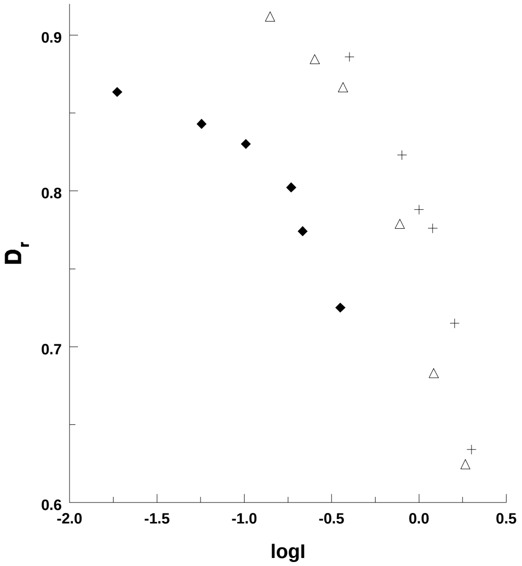
Figure 2. (a) The relative TMA$^+$ self-diffusion coefficient, D_r, against the logarithm of PMA concentration, $\log(c_p)$, at a degree of neutralization, $\alpha = 0.8$, with added MgCl$_2$. The charge normalized ratio of counterions of the added salt and counterions of the polyions, Y, is constant over the concentration range. □, $Y \approx 0$; ▼, $Y = 0.21$; ○, $Y = 0.41$; ◆, $Y = 0.61$. The lines are drawn as guides to the eye. (b) The relative monovalent counterion self-diffusion coefficient, D_r, calculated with the PBS model against the logarithm of polyion concentration, $\log(c_p)$, with added bivalent 2–1 salt. The ratio of counterions of the added salt and counterions of the polyions, Y, is constant over the concentration range, distance of closest approach, $a = 6$ Å, distance between charges on the chain, $b = 3.13$ Å. Dashed curve, $Y = 0$; dashed-dotted curve, $Y = 0.2$; dotted curve, $Y = 0.4$; full curve, $Y = 0.6$.



(a)

(b)

Figure 3. (a) The polyion concentration, $c_{p,max}$, at the maximum TMA$^+$ relative counterion self-diffusion coefficient, $D_{r,max}$ against the charge normalized ratio of counterions of the added salt and of the polyions, Y, in PMA solutions at a degree of neutralization, $\alpha = 0.8$, with added TMACl or $MgCl_2$. □, added TMACl; ▼, added $MgCl_2$. The lines are drawn as guides to the eye. (b) The maximum relative TMA$^+$ self-diffusion coefficient, $D_{r,max}$, against the ionic strength at the maximum, I_{max}, in PMA solutions at a degree of neutralization, $\alpha = 0.8$, with added TMACl or $MgCl_2$. □, added TMACl; ▼, added $MgCl_2$. (c) The relative TMA$^+$ self-diffusion coefficient, D_r, against the logarithm of ionic strength, $\log I$, in 0.017 monomol kg^{-1} PMA solutions at a degree of neutralization, $\alpha = 0.8$, with added TMACl or $MgCl_2$. The ratio of counterions of the added salt and counterions of the polyions, Y, is constant over the concentration range. △, added TMACl, $Y = 10$; ◆, added $MgCl_2$, $Y = 0.61$; +, D_r(TMA$^+$) in TMACl solutions in D_2O.



(c)

Figure 3. (Continued)

Figure 3(b) shows the plot of $D_{r,max}$ against the ionic strength at the maximum, I_{max} ($I_{max} = (1/2)c_{p,max}\alpha(1 + nY)$; $n = 2$ with monovalent 1–1 added salt and $n = 3$ with bivalent 2–1 added salt). $D_{r,max}$ decreases with increasing ionic strength. Addition of salt lowers $c_{p,max}$ to such an extent that a lower I_{max} results in the present range of Y values. At $c_{p,max}$, where the electrostatic and obstruction effects on D_r are in balance, D_r depends on the valence of the added salt only through the Debye screening length, κ^{-1} ($\kappa^2 = 2e^2/(\varepsilon_0\varepsilon_r kT) \times I$).

At the highest ratio of added salt to polyion $D_{r,max}$ has disappeared, for both monovalent 1–1 salt ($Y = 10$) and bivalent 2–1 salt ($Y = 0.6$). If, for these Y values, D_r is plotted against ionic strength, together with the ionic strength dependence of the relative TMA$^+$ self-diffusion coefficient in TMACl solutions in D_2O, it shows (figure 3(c)) that D_r(TMA–PMA, $Y = 10$) hardly differs from D_r(TMACl) confirming the vanishing electrostatic disturbance by the polyion. In the same figure the curve of ionic strength dependence of the relative TMA$^+$ self-diffusion coefficient in PMA solutions with added $MgCl_2$ ($Y = 0.6$) is similar in shape to the curves of the ionic strength dependence of D_r(TMA$^+$) in TMA–PMA/TMACl at a value of $Y = 10$ and D_r(TMA$^+$) in TMA chloride solutions. The typical polyion effect, the maximum relative counterion self-diffusion coefficient against polyelectrolyte concentration, has disappeared.

In figure 4, D_r of TMA$^+$ in polyion solutions at a PMA concentration of $c_p \approx 0.017$ mol kg^{-1} has been displayed against the charge normalized ratio of counterions of added salt and counterions of the polyion, Y. Also plotted are the values of D_r calculated with the PBS model. The increase of D_r with Y is much larger in the presence of excess 2–1 salt than if 1–1 salt is added to the solution, both for the calculated and measured self-diffusion coefficients. This is also true for the ionic strength dependence of D_r. Contrary to $D_{r,max}$ the relative counterion self-diffusion coefficient does depend on the valency of the counterions of the added salt. Calculated self-diffusion coefficients are too high and the increase with Y (and I, for that matter) is smaller than in experiment. Also the data (tables 1

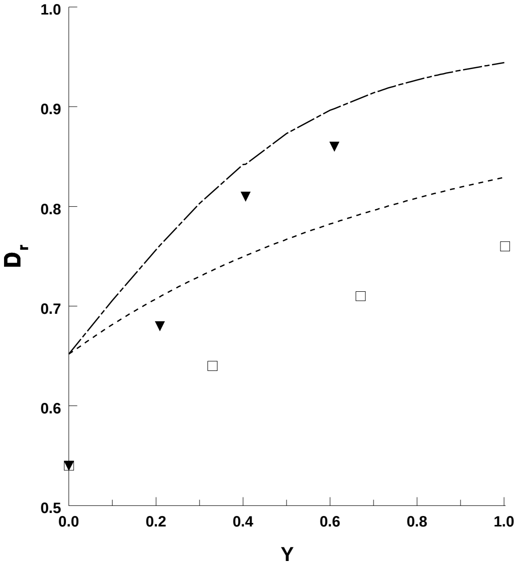


Figure 4. The relative TMA$^+$ self-diffusion coefficient, D_r, against the charge normalized ratio of counterions of the added salt and of the polyions, Y, in PMA solutions at a degree of neutralization, $\alpha = 0.8$ and a polymer concentration, $c_p = 0.017$ mol kg^{-1}, with added TMACl or MgCl$_2$ and values calculated with the PBS model, distance of closest approach, $a = 6$ Å, distance between charges on the chain, $b = 3.13$ Å. □, added TMACl; ▼, added MgCl$_2$; dashed curve, added monovalent 1–1 salt; dashed-dotted curve, added bivalent 2–1 salt.

and 2) show that the quantitative differences between model calculations and experiment grow with polyion concentration. Qualitative agreement is good, however. On increasing c_p the dependence of D_r on Y gets smaller as is correctly predicted by the model.

In figure 5 the dependence of D_r(TMA$^+$) on Y with added monovalent salt (TMACl) in PMA solutions is plotted for two polyelectrolyte concentrations ($c_p \approx 0.017$ mol kg^{-1} and $c_p \approx 0.15$ mol kg^{-1}), together with the predictions from CC and PBS theory. Data are collected in table 3. From the figure it becomes clear that up to $Y = 0.3$ D_r is smaller for lower polyion concentrations. At $Y \approx 0.7$ $D_r(c_p \approx 0.017)$ equals $D_r(c_p \approx 0.15$ mol kg^{-1}). Above this value the two curves diverge. The dependence of D_r on ionic strength at the lowest concentration, $c_p \approx 0.017$ mol kg^{-1}, is an increasing function of Y. At the highest concentration, $c_p \approx 0.15$ mol kg^{-1}, D_r decreases with Y above $Y \approx 2$. The maximum D_r against Y does not occur at lower polyion concentrations and can be explained as the balance between the effects on the counterion dynamics of the screening of the polyion potential by excess salt and the high concentration of added salt. At lower polyion concentrations the maximum will occur at Y values that were not studied in this experiment ($Y > 10$).

The Y-dependence of D_r calculated with CC theory agrees, at low polyion concentrations, quantitatively better with experiment than that calculated with the PBS model. Both theories treat the counterion motion in electrostatic equipotential surfaces of the polyion as undisturbed, which gives rise to too high counterion self-diffusion coefficients. In CC theory condensed counterions are immobile at charge densities higher than one (or, in fact, diffuse with a self-diffusion coefficient equal to that of the polyion), thus reducing the calculated counterion self-diffusion coefficient. Magdelenat *et al* [7] already showed, however, that the concept of immobile condensed counterions is an oversimplified

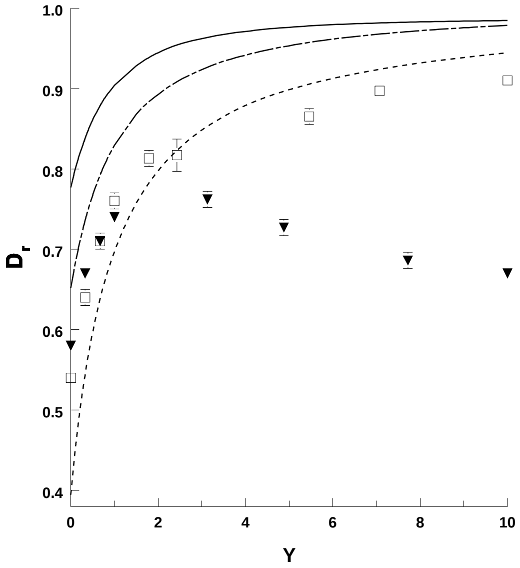


Figure 5. The relative TMA$^+$ self-diffusion coefficient, D_r, against the ratio of counterions of the added salt and of the polyions, Y, in PMA solutions at a degree of neutralization, $\alpha = 0.8$ and polymer concentrations, $c_p = 0.017$; 0.15 mol kg^{-1}, with added TMACl and the values calculated with CC and PBS theory (charge density parameter, $\xi = 2.28$; distance of closest approach, $a = 6$ Å, distance between charges on the chain, $b = 3.13$ Å). □, $c_p = 0.017$ mol kg^{-1}; ▼, $c_p = 0.15$ mol kg^{-1}; dashed curve, CC theory; dashed-dotted curve, PBS theory ($c_p = 0.017$ mol kg^{-1}); full curve, PBS theory ($c_p = 0.15$ mol kg^{-1}).

representation of reality.

The predictions from PBS theory are qualitatively correct up to $Y = 0.3$. $D_r(Y)$ is lower at lower polyion concentrations, although calculated values are systematically too high. The divergence of the two curves at higher Y cannot be explained by PBS theory, for the only obstruction taken into account is caused by the polyion. Instead the model predicts that, at higher values of Y, the dependence on polyion concentration gradually disappears.

5. Conclusions

The concentration dependence of the counterion self-diffusion coefficient in polyelectrolyte solutions at varying ionic strength is qualitatively well described with the PBS model in the cylindrical cell for polyions. In accord with calculations the maximum of D_r against concentration was found at lower polyion concentrations and with a higher value if the ionic strength was increased. This agrees with the assumption that the maximum is due to a combination of the obstruction effect and the electrostatic influence of the polyion on counterion dynamics. The value of the relative counterion self-diffusion coefficient at the maximum is independent of the valence of the added salt, but depends on the Debye screening length.

At fixed polyion concentration but different ratios of added salt and counterions, Y, PBS calculations on D_r are in qualitative agreement for both added monovalent 1–1 salt and bivalent 2–1 salt, but the experimental increase of D_r on increase of the ratio of added salt and polyelectrolytes is larger than calculated, indicating that the calculated electric field of the polyion has too long a range. With monovalent added salt the dependence of D_r on Y offered by CC theory is in better quantitative agreement with experiment than the PBS model, at least at low-polyion concentrations. This is reminiscent of the fact that, although both theories assume undisturbed motion in electrostatic equipotential surfaces of the polyion, leading to too high counterion self-diffusion coefficients, only CC theory presumes that a fraction of counterions becomes immobile at higher charge densities, thus reducing the calculated self-diffusion coefficient.

A maximum D_r against Y was observed upon addition of monovalent 1–1 salt at higher polyion concentrations, that could be explained to arise as a combination of the decreasing electrostatic influence of the polyion on the counterion dynamics, because of screening upon addition of salt and concentration effects of the added salt. This maximum is not predicted by either the PBS or the CC model, because concentration effects of the added salt are not taken into account by these models.

References

[1] Schipper F J M, Hollander J G and Leyte J C 1997 *J. Phys.: Condens. Matter* **9** 11 179
[2] Yoshida N 1978 *J. Chem. Phys.* **69** 4867
[3] Nilsson L G, Nordenskiöld L, Stilbs P and Braunlin W H 1985 *J. Phys. Chem.* **89** 3385
[4] Manning G S 1969 *J. Chem. Phys.* **51** 924
[5] Stejskal E O 1965 *J. Chem. Phys.* **43** 3597
[6] Mills R 1973 *J. Phys. Chem.* **77** 685
[7] Magdelenat H, Turq P and Chemla M 1974 *Biopolymers* **13** 1535