

## Mass transport in polyelectrolyte solutions

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 1409

(<http://iopscience.iop.org/0953-8984/11/6/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.214

The article was downloaded on 15/05/2010 at 06:58

Please note that [terms and conditions apply](#).

## Mass transport in polyelectrolyte solutions

F J M Schipper and J C Leyte

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

Received 2 October 1998, in final form 15 December 1998

**Abstract.** The self-diffusion coefficients of the three components of a salt-free heavy-water solution of polymethacrylic acid, completely neutralized with tetra-methylammonium hydroxide, were measured over a broad concentration range. Three concentration regions were observed for the self-diffusion of both the polyions and the counterions. At polyion concentrations below 0.01 mol monomer  $\text{kg}^{-1}$ , the dilute concentration regime for the polymer, the polyion self-diffusion coefficient approaches the self-diffusion coefficient of a freely diffusing rod upon dilution. At polyelectrolyte concentrations above 0.1 mol monomer  $\text{kg}^{-1}$ , the self-diffusion coefficients of the solvent, the counterions and the polymer decreased with concentration, suggesting that this decrease is due to a topological constraint on the motions of the components. In the intermediate-concentration region, the self-diffusion coefficients of the polyions and the counterions are independent of the concentration. The polyion dynamic behaviour is, in the intermediate- and high-concentration regions, reasonably well described by that of a hard sphere, with a radius of 3.7 nm. A correct prediction for the solvent dynamics is given by the obstruction effect of this hard sphere on the solvent. The relative counterion self-diffusion coefficient is predicted almost quantitatively over the entire concentration range with the Poisson–Boltzmann–Smoluchowski model for the spherical cell, provided that the sphere radius and the number of charges are chosen appropriately (approximately the number of charges in a persistence length). Using this model, the dependence of the counterion self-diffusion coefficient on the ionic strength, polyion concentration and counterion radius is calculated quantitatively over a large concentration range.

### 1. Introduction

In previous publications [1, 2] it has been shown that there are three regions in the concentration profile of the relative counterion self-diffusion coefficient,  $D_r$  ( $D_r = D/D_0$ ,  $D_0 = kT/\eta$ ;  $\eta$  is the viscosity of the pure solvent). A dilute region was found at polyion concentrations,  $c_p$ , lower than 0.01 mol monomer  $\text{kg}^{-1}$  (mol  $\text{kg}^{-1}$ ), where the interactions between the counterions and the polyions vanish and  $D_r$  approaches the limiting value of unity upon dilution. At concentrations higher than approximately 0.1 mol  $\text{kg}^{-1}$ ,  $D_r$  decreases upon concentration, because of a topological constraint of the polyion on the counterion dynamics. In the intermediate-concentration region,  $D_r$  is concentration independent and the counterion dynamics is governed by the electrostatic interactions with the polyions. In theoretical considerations [3–5] of polyelectrolytes in solution, the existence of different concentration regimes is presumed. As is the case for counterions, the existence of at least two polyion concentration regimes has been confirmed experimentally [6, 7].

In this paper the dependence on polyion concentration of the mass transport of the three constituents of a salt-free polyelectrolyte solution, polyions, counterions and solvent, is discussed. Measurement of the polyion, counterion and solvent self-diffusion coefficient over a concentration range which covers as many concentration regions as possible might give insight

into the mechanisms that govern the dynamic processes in each region. It must be realized that although the polyion and counterion dynamics are coupled, through the dependence of the fluxes on each other, the coupling constants are, because of the difference in magnitude of the polyion and counterion self-diffusion coefficients, very small and a quantitative connection is almost impossible to obtain. We shall compare the concentration profiles of the self-diffusion coefficients of the different components only on a qualitative basis.

Here we report a PFG-NMR (pulsed-field-gradient nuclear magnetic resonance) self-diffusion study on a salt-free solution of completely neutralized polymethacrylic acid (PMA). A short PMA fragment of only 90 monomers was chosen to measure self-diffusion coefficients in different polyion concentration regimes. Tetra-methylammonium ( $\text{TMA}^+$ ) was chosen as the counterion, because it has magnetic spin characteristics that are very convenient in a PFG-NMR experiment. The TMA–PMA was dissolved in deuterium oxide and not in water, because the  $^1\text{H}$  NMR signal of the abundant water would overlap with both the PMA and  $\text{TMA}^+$  signals and thus make the measurement of the self-diffusion coefficients of the individual components very intricate.

## 2. Experimental procedure

The sodium salt of PMA (polymethacrylic acid) with a narrow molecular weight distribution was purchased from Polymer Standard Services. It consisted of a weight-averaged number ( $N_W$ ) of 89 monomers and a number-averaged number ( $N_N$ ) of 85 monomers. A solution of the PMA was acidified by addition of an excess of a hydrochloric acid solution (Merck Titrisol, 0.1 N). Separation of the resulting acidic PMA and sodium chloride together with the remains of the hydrochloric acid was achieved by repetitive dialysis with freshly deionized water. The external solvent was, after dialysis, checked against a blank with a carbon analyser (Ionic Incorporated 1555B) for amounts of carbon larger than the amount of carbon in the dissolved carbon dioxide, which would be an indication that PMA comes through the pores of the dialysis bags. No organic carbon was detected. Dialysis was repeated until the conductivity of the external solvent, after equilibration, equalled that of water ( $\Lambda \approx 1 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ , at room temperature). The acidic PMA was neutralized to a degree of neutralization  $\alpha = 1.0$  with a solution of tetra-methylammonium hydroxide (TMAOH). Before use, the TMAOH had been decarboxylated with an anionic exchange resin in the hydroxide form. The acid–base titration curve of the TMAOH solution showed only one point of equivalence, indicating that any carbon dioxide had been successfully removed.

Since the chemical shift between water and  $\text{TMA}^+$  is small ( $\sim 2$  ppm) and signal overlap would prevent the measurement of the  $\text{TMA}^+$  self-diffusion coefficient by means of PFG-NMR,  $\text{D}_2\text{O}$  was chosen as the solvent for the TMA–PMA. To remove the water, the aqueous TMA–PMA solution was frozen and the solvent was evaporated under a high vacuum. To further reduce the water content, dry TMA–PMA was dissolved in  $\text{D}_2\text{O}$ , frozen and again evaporated under a high vacuum. This procedure was repeated until the water content of the samples was smaller than 0.5% and the signals of water and  $\text{TMA}^+$  could be separated spectroscopically. Finally, TMA–PMA samples in  $\text{D}_2\text{O}$  were prepared over a large polymer concentration range.

Self-diffusion PFG-NMR measurements were carried out using a Bruker AM200 wide-bore magnet, connected to a Bruker Aspect 3000 spectrometer, at a constant temperature of  $25 \pm 0.1$  °C, kept constant with a gas thermostat. The sample height in the NMR tubes was in the range 6–8 mm, so the entire sample experienced a homogeneous magnetic field gradient. A Techtron 7570 amplifier, coupled to the spectrometer, supplied practically rectangular gradients (from  $G = 0$  to  $G_{\text{max}}$  and back within a constant time of about 100  $\mu\text{s}$ ), of a duration  $\delta$  of a few milliseconds. The measurement of the self-diffusion coefficients of PMA and  $\text{TMA}^+$  was

carried out at a magnetic field gradient of  $G = 0.36 \text{ T m}^{-1} \text{ A}^{-1}$  at a maximum current of 20 A, generated by an actively shielded gradient coil (built at Massey University, Palmerston North, New Zealand, by the group of Professor P T Callaghan), at a field strength corresponding to a resonance frequency of 200.132 MHz for the  $^1\text{H}$  nuclei. Because of the inequality of the longitudinal and transverse relaxation rates, the stimulated spin-echo method [8] was used. The duration of the gradient pulses was 2 ms for the measurement of the  $\text{TMA}^+$  self-diffusion coefficient and 3 ms for PMA. The time between the pulses ( $\Delta$ ) was 20 ms in both cases. After each gradient pulse there 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 rf pulse or the signal accumulation.

For the measurement of the  $\text{D}_2\text{O}$  self-diffusion coefficient, use was made of a probe (Doty Scientific, Incorporated), which generated a gradient of  $0.4 \text{ T m}^{-1} \text{ A}^{-1}$  at a maximum current of 20 A and a resonance frequency of 30.722 MHz for the  $^2\text{D}$  nuclei. The transverse and longitudinal relaxation rates were equal, so the conventional spin-echo [9] method was used. The duration of the gradient pulses and the time between them were 2.5 and 20 ms, respectively. The amplitude,  $A_G$ , of the Fourier transform of the acquired signal (not showing any significant deformation, suggestive of remnant gradients or pulse displacement) is given by

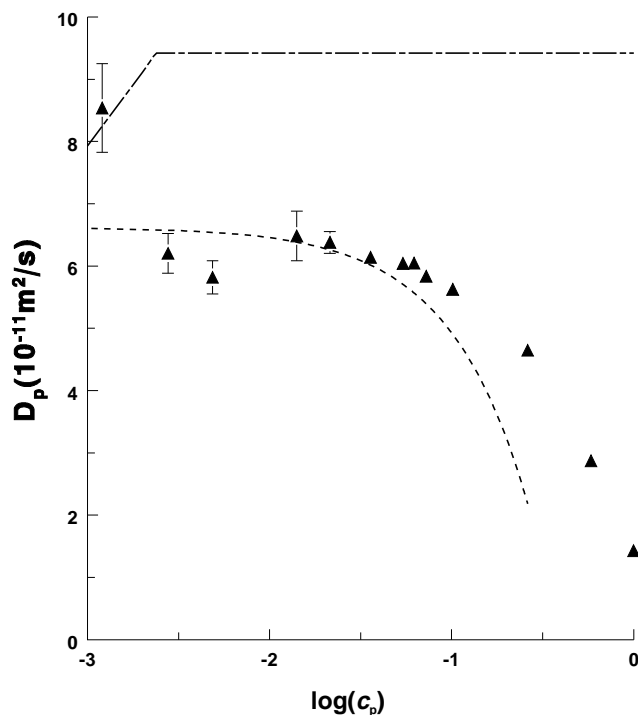
$$A_G = A_0 x \exp\left[-\gamma^2 G^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right) x D\right] \quad (1)$$

with  $A_0$  the echo amplitude at zero gradient,  $\gamma$  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. Typically 30 gradient values were used to determine the self-diffusion coefficient. The values were chosen in such a way that  $G^2$  increased linearly. At the highest gradient value, the echo attenuation was typically a factor of  $e^{+4}$ .

### 3. Results

In figure 1 the polyion self-diffusion coefficient  $D_p$  of completely neutralized PMA consisting of 90 monomers in  $\text{D}_2\text{O}$  is plotted as a function of the polyion concentration. Three concentration regions can be distinguished. There are a dilute and a concentrated region (from monomer concentration  $c_p \approx 0.001$  to  $0.01 \text{ mol kg}^{-1}$  and from  $c_p \approx 0.1$  to  $1 \text{ mol kg}^{-1}$ , respectively), in which  $D_p$  decreases upon concentration, and an intermediate-concentration region, where  $D_p$  hardly varies with polyion concentration, but does depend on the ionic strength and the degree of neutralization [10, 11]. In the low-concentration region,  $D_p$ , upon dilution, approaches the self-diffusion coefficient of a hard rod, with the same dimensions as the polyion at infinite dilution, assuming the vinylic monomer length to be  $1.7 \text{ \AA}$  ( $D_p = 1.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ; rod diameter:  $5 \text{ \AA}$  [12]). A shorter monomer length than  $2.5 \text{ \AA}$ , which had already been suggested by Aver and Alexandrowitz [13] to explain osmotic pressure measurements on PSS (polystyrene sulphonate) solutions [12], another vinylic polyion with the same monomer length as fully charged PMA, was found by Kassapidou *et al* [14] to be  $1.7 \text{ \AA}$ . Although the dimensions of the polyion chains decrease upon concentration in the dilute region, the polyion self-diffusion coefficient decreases as well. This must reflect the growing interactions between the chains.

The polyion concentration at the boundary of the dilute and the intermediate-concentration regions ( $c_p \approx 0.01 \text{ mol kg}^{-1}$ ) conforms with the crossover concentration  $c^*$  between the dilute and semidilute concentration regimes as predicted by Odijk [3] ( $c^* = 0.004 \text{ mol l}^{-1}$  and  $c^* = 0.018 \text{ mol l}^{-1}$ , with and without the assumption of counterion condensation). The decrease of  $D_p$  around a polyion concentration of  $c_p \approx 0.1 \text{ mol kg}^{-1}$  conforms with the next molecular-weight-independent crossover concentration ( $c^{**} \approx 0.06 \text{ mol l}^{-1}$ , without



**Figure 1.** The PMA self-diffusion coefficient,  $D_p$ , versus the logarithm of the PMA concentration,  $\log(c_p)$ , for salt-free, completely neutralized solutions of PMA consisting of 90 monomers in  $\text{D}_2\text{O}$ . The dashed curve represents the self-diffusion coefficient of a hard sphere ( $R_{\text{HS}} = 3.7 \text{ nm}$ ) in a hard-sphere suspension; the dashed-dotted line is the polyion self-diffusion coefficient as calculated using the electrostatic blob model.

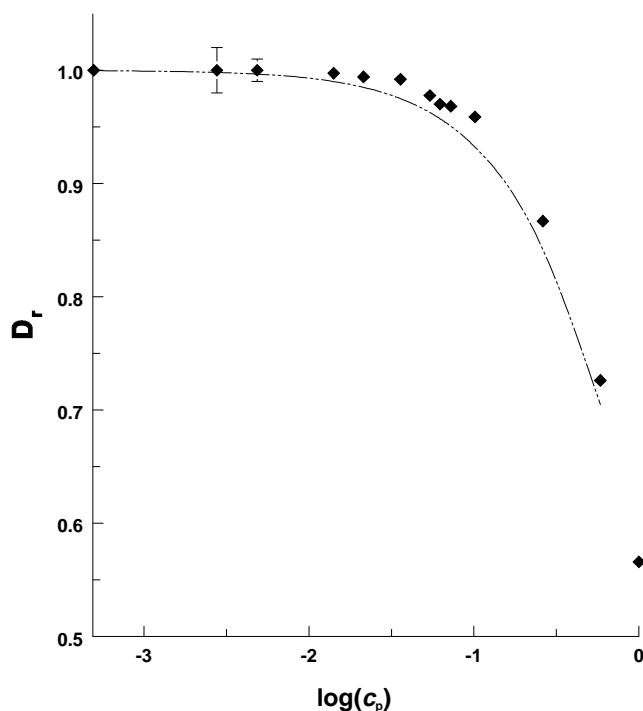
assuming counterion condensation). Comparison with the literature [15–17] reveals, however, that the decrease of  $D_p$  upon concentration in the high-concentration region that is found for vinylic polymers is dependent on the molecular weight. This would imply that the chains are not entangled at these concentrations, which is in better agreement with the electrostatic blob model [5] or with the wormlike-chain model as employed by Kaji *et al* [18, 19] than with the Odijk scaling relations [3] that presume the existence of a network at these concentrations.

In analogy with the explanation of the maximum relative counterion self-diffusion coefficient as a function of polyion concentration, which is a result of the competition between electrostatic and topological effects [1], the experimental data at intermediate and high concentrations (from  $c_p \approx 0.01$  to  $1 \text{ mol kg}^{-1}$ ) can be explained as follows. Although the dimensions of the chains are decreasing, the electrostatic interactions between the chains get stronger, giving rise to a constant polyion self-diffusion coefficient over a certain concentration range. Of course, other explanations are possible. If a lattice-like structure is presumed [3], the polyion self-diffusion coefficient depends on the reptation time in the lattice. Upon concentration, the strengths of the electrostatic interactions increase, but the lattice dimension decreases, which could also give rise to a concentration-independent self-diffusion coefficient. At higher concentrations, next to the electrostatic interactions, the mutual physical obstruction of the polyions, together with possible entanglements, become important, resulting in a decay of  $D_p$  upon concentration at concentrations higher than  $c_p \approx 0.1 \text{ mol kg}^{-1}$ .

The diffusion data at intermediate concentrations are reasonably well described by the

concentration dependence of the self-diffusion coefficient of a hard sphere with a constant radius ( $R_{\text{HS}} = 3.7$  nm) in a hard-sphere suspension, as calculated with a modified molecular dynamics simulation [20], suggesting a sphere-like conformation of the polyions at these concentrations ( $0.01 \text{ mol kg}^{-1} < c_p < 0.1 \text{ mol kg}^{-1}$ ). In the intermediate region almost quantitative agreement was found, while in the concentrated region the polyion diffusive behaviour is still predicted correctly qualitatively. A polyion in solution is not a hard sphere and cannot—especially at high concentrations, where the chains overlap—be expected to act as a hard sphere. It is therefore surprising that a hard-sphere description yields such good results. Although the end-to-end distance of a polyion in solution is of course not an adjustable parameter, the hard-sphere radius is in reasonable agreement with experimental findings on the end-to-end radius of vinylic polyions [18, 21].

Dobrynin *et al* [5] employ their scaling theory for polyelectrolyte solutions (the blob model) to explain experimental data for static and dynamic properties of (vinylic) PSS in solution by adjusting the PSS charge density, or the number of monomers between charges, to accommodate the data. The best quantitative agreement between the blob model and our experiments on the concentration dependence of the self-diffusion coefficient of fully charged PMA in solution is obtained when the number of monomers between charges has the minimum value of one, resulting in a blob that is not very realistic, with a size smaller than the monomer size (1.1 Å). Although the blob model correctly predicts the existence of a concentration range where  $D_p$  is concentration independent, albeit with too high a value, the predicted decrease of the polyion self-diffusion coefficient upon dilution in the dilute concentration regime was not



**Figure 2.** The relative solvent self-diffusion coefficient,  $D_r$ , versus the logarithm of the PMA concentration,  $\log(c_p)$ , for salt-free, completely neutralized solutions of PMA consisting of 90 monomers in  $\text{D}_2\text{O}$ . The dashed–dotted curve represents the calculated obstruction effect of a hard sphere ( $R_{\text{HS}} = 3.7$  nm) on the self-diffusion coefficient of the solvent.

confirmed by our experiments (figure 1). The quantitative differences between the calculated polyion self-diffusion coefficient and experiment in the concentration-independent region diminish if the monomer size is taken as 2.5 Å instead of 1.7 Å, but the qualitative picture remains inadequate.

In figure 2 the relative self-diffusion coefficient,  $D_r$ , of the solvent in the same solution as above (completely neutralized TMA–PMA consisting of 90 monomers in D<sub>2</sub>O, without any additional salt) has been plotted against the logarithm of the polyion concentration. The relative solvent self-diffusion coefficient starts to decrease strongly with polyion concentration at polymer concentrations around  $c_p \approx 0.1 \text{ mol kg}^{-1}$ ; at the same concentration the polyion self-diffusion coefficient starts to decrease upon concentration. A decrease of the relative solvent self-diffusion coefficient upon concentration is usually referred to as an obstruction effect [22]: a shortening of the diffusive path caused by obstructing particles in the solution. Also displayed in the figure is the obstruction effect of a hard sphere with a radius of 3.7 nm (equal to that used to calculate the polyion self-diffusion coefficient) on the relative solvent self-diffusion coefficient as calculated using the PBS model for a spherical cell [23]:

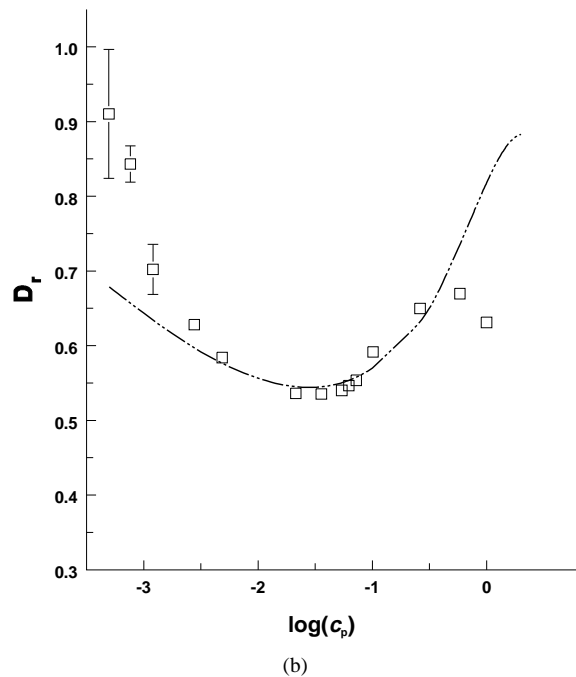
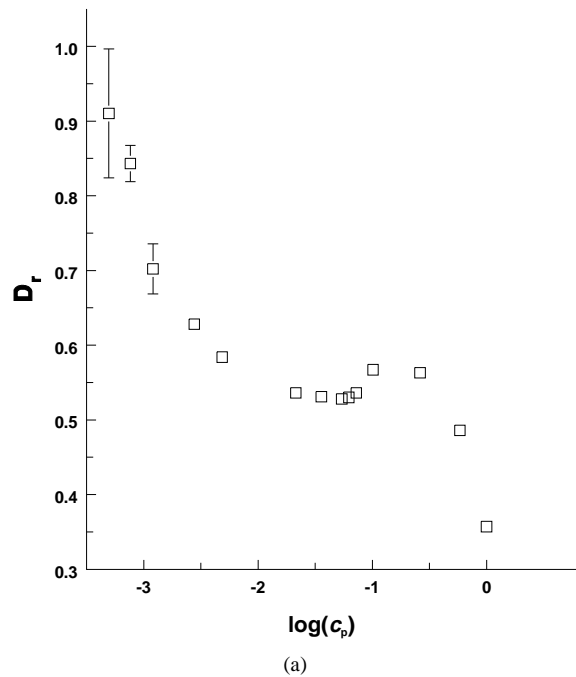
$$D_r = \left(1 + \frac{1}{2}\Phi\right)^{-1} \quad (2)$$

where  $F$  is the volume fraction of spheres. A fair agreement with experiment is found over the entire polyion concentration range. It must be noted, however, that an identical concentration dependence of the solvent self-diffusion coefficient was found for solutions of TMA–PMA of higher molecular weight [1]. A polyion is not a hard sphere, since both solvent molecules and counterions can penetrate the polyelectrolyte coil, so it is remarkable that the solvent diffusion data can be predicted so accurately with a hard-sphere model. Apparently, the solvent is more hindered by the polyion than would be expected on the basis of the geometrical size of the polymer alone.

In figure 3(a) the relative self-diffusion coefficient of TMA<sup>+</sup> in a salt-free solution of completely neutralized PMA consisting of approximately 90 monomers in D<sub>2</sub>O is plotted against the logarithm of the polyion concentration. (These data have been published previously [24].) A remarkable resemblance between the concentration dependence of the relative counterion self-diffusion coefficient,  $D_r$ , and that of the polymer self-diffusion coefficient,  $D_p$ , is observed. Three concentration regions can be distinguished, with the same boundary concentrations as were found for the polymer self-diffusion. A low-concentration region exists ( $c_p < 0.01 \text{ mol kg}^{-1}$ ), where the interactions between the counterions and the polyions gradually disappear upon dilution and  $D_r$  approaches unity. This increase of  $D_r$  upon dilution in the low-concentration region has also been found, at the same concentration, for solutions of polyions of higher molecular weight [1, 25, 26], but here, since we know that the polyion starts to behave as a rod at these concentrations, this must be partially attributed to polyion end effects on the counterion self-diffusion [27].

There is also an intermediate concentration-independent region ( $0.01 \text{ mol kg}^{-1} < c_p < 0.1 \text{ mol kg}^{-1}$ ) where  $D_r$  is governed by electrostatics [2]. In the high-concentration region ( $c_p > 0.1 \text{ mol kg}^{-1}$ )  $D_r$  decreases with concentration, as was found for the polyion and the solvent self-diffusion coefficient, and this is ascribed to the physical obstruction by the polyion.

It has already been pointed out [1] that at intermediate and high polyion concentrations there is qualitative agreement between experimental counterion self-diffusion coefficients and those calculated using the PBS model for the cylindrical cell [28, 29]. At PMA concentrations below 0.01 monomol kg<sup>-1</sup> the TMA<sup>+</sup> self-diffusion coefficient starts to increase strongly upon dilution. This increase is not found using the cylindrical PBS model, because of the long range of the electrostatic potential of an infinitely long charged rod, and depends on both polyion



**Figure 3.** (a) The relative  $\text{TMA}^+$  self-diffusion coefficient,  $D_r$ , versus the logarithm of the PMA concentration,  $\log(c_p)$ , for salt-free, completely neutralized solutions of PMA consisting of 90 monomers in  $\text{D}_2\text{O}$ . (b) The relative  $\text{TMA}^+$  self-diffusion coefficient,  $D_r$ , corrected for the self-diffusion coefficient for the solvent, versus the logarithm of the PMA concentration,  $\log(c_p)$ , for salt-free, completely neutralized solutions of PMA consisting of 90 monomers in  $\text{D}_2\text{O}$ . The dashed-dotted curve represents the relative counterion self-diffusion coefficient calculated using the PBS model for spherical symmetry ( $R_s = 1 \text{ nm}$ ,  $N_q = 20$ ).



end effects and the persistence length [24].

From the ionic and polyelectrolyte concentration dependences of the polyion persistence length for vinylic polyions, which can be extracted from neutron scattering data, an expression for the persistence length in terms of the Debye length can be derived (in nanometres [14, 19, 30–32]):

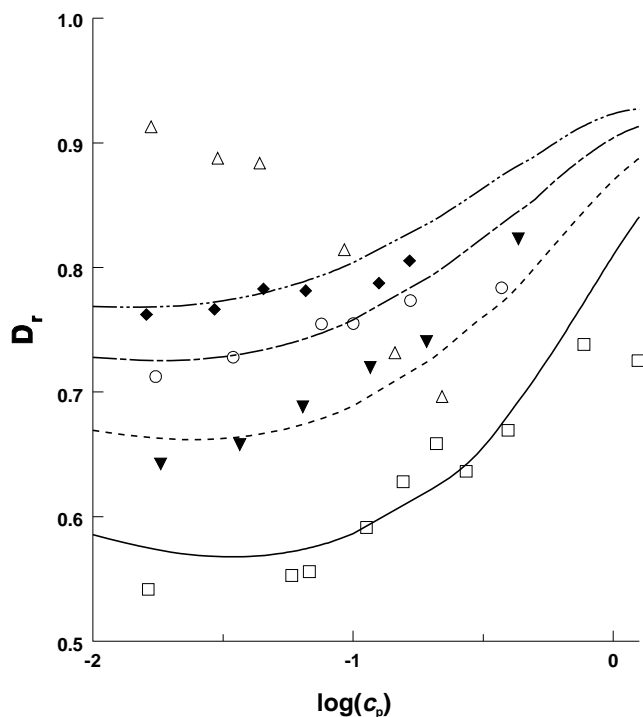
$$L_p = 10^{2/3} \kappa^{-2/3} \text{ nm} \quad (3)$$

in which the Debye screening length,  $\kappa^{-1}$ , is defined by

$$\kappa^2 = [e^2 / (\epsilon_0 \epsilon_r k T)] \sum n_i z_i^2$$

where  $e$  is the protonic charge,  $\epsilon_0$  and  $\epsilon_r$  are the permittivity of the vacuum and the relative permittivity, respectively,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $n_i$  and  $z_i$  are the number concentration and the valence of the small ions  $i$  in the solution. The ratio of the experimentally obtained persistence length and the Debye screening length is a decaying function of the polyion concentration. Accordingly, the assumption of cylindrical symmetry of the polyion becomes less accurate upon dilution, since the Debye atmosphere expands at a faster rate than the polyion stiffens.

Therefore the assumption that the polyion electric field, as experienced by the counterions, can be represented by the electric field of a charged sphere will be tested and the counterion



**Figure 4.** The relative  $\text{TMA}^+$  self-diffusion coefficient,  $D_r$ , corrected for the self-diffusion coefficient for the solvent, versus the logarithm of the PMA concentration,  $\log(c_p)$ , at a degree of neutralization  $\alpha = 0.8$ , with added TMACl. The ratio of the number of counterions of the added salt to the number of counterions of the polyions,  $Y$ , is constant over the concentration range.  $\square$ :  $Y \approx 0$ ;  $\blacktriangledown$ :  $Y = 0.33$ ;  $\circ$ :  $Y = 0.67$ ;  $\blacklozenge$ :  $Y = 1.0$ , together with the calculated values [23] ( $R_s = 1 \text{ nm}$ ,  $N_q = 18$ ).

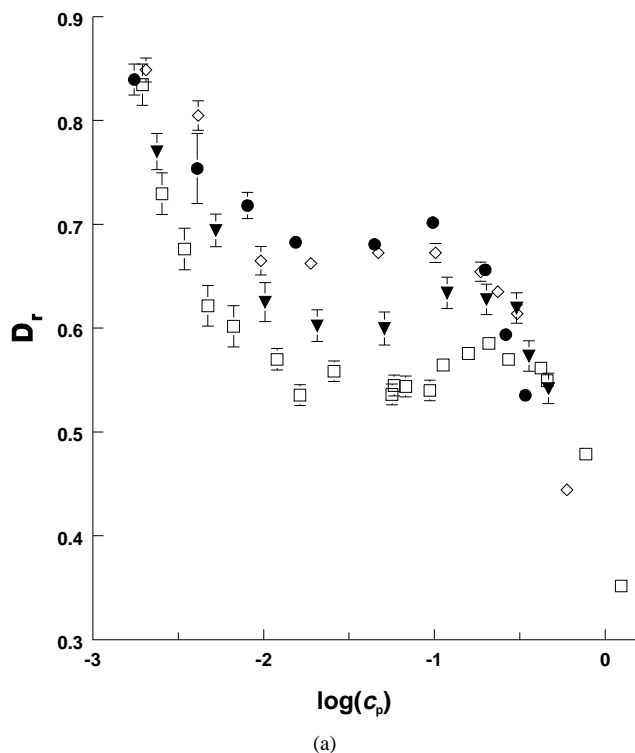
self-diffusion coefficient will be calculated using the PBS model for a spherical cell [23]. A brief outline of the model is given in the appendix.

In the PBS model the solvent is treated as an unperturbed dielectric, although it was observed that the solvent self-diffusion coefficient depends on the polyion concentration (figure 2). If the experimental counterion self-diffusion coefficient is corrected for the self-diffusion coefficient of the solvent at that concentration (by simply dividing the relative counterion self-diffusion coefficient by the relative solvent self-diffusion coefficient), quantitative agreement of the PBS model for the spherical cell with experiment is found over a large range and qualitative agreement over the entire polyion concentration range (figure 3(b)). The hard-sphere radius,  $R_s = 1$  nm, and the number of charges on the sphere,  $N_q = 20$ , were chosen to accommodate the data, but at a surface charge density approximately equal to that chosen for the cylindrical case [2]. Note that  $N_q$  is of the order of the number of charges in a persistence length,  $L_p$ . After correction for the solvent self-diffusion coefficient, the maximum relative counterion self-diffusion coefficient is found at higher polyion concentrations. The maximum arises due to the combination of the effects of physical obstruction and electrostatic disturbance on the counterion dynamics [1]. The solvent apparently acts as an additional obstruction to the motion of the counterions.

In figures 4 and 5 we present some previously published data [1, 2], which we discuss here in terms of the PBS model for the spherical cell. In figure 4 the relative TMA<sup>+</sup> self-diffusion coefficient for solutions of PMA, containing approximately 1000 monomers, at a degree of neutralization  $\alpha = 0.8$ , has been plotted against the logarithm of the polyion concentration. The ratio of the number of added salt counterions to the number of polyionic counterions,  $Y$ , has been varied from  $Y = 0$  to  $Y = 1$  and was constant over the concentration range. The measured self-diffusion coefficients have been corrected for the solvent self-diffusion coefficients as described above. In order to fit the data to the model, we chose again a hard-sphere radius,  $R_s$ , of 1 nm and a number,  $N_q$ , of 18 charges. All of the data can be fitted almost quantitatively over the entire polyion concentration range. The increase of  $D_r$  with the ionic strength is very well predicted.

In figure 5(a) the self-diffusion coefficients of four TAA<sup>+</sup> (tetra-alkylammonium) ions in solutions of PMA (1000 monomers,  $\alpha = 0.8$ ) in D<sub>2</sub>O are plotted against the logarithm of the polyion concentration (tetra-methylammonium, TMA<sup>+</sup>, counterion radius [33]:  $R_c \approx 3.5$  Å; tetra-ethylammonium, TEA<sup>+</sup>,  $R_c \approx 4.5$  Å; tetra-propylammonium, TPA<sup>+</sup>,  $R_c \approx 4.5$  Å; tetra-butylammonium, TBA<sup>+</sup>,  $R_c \approx 5.5$  Å). A minimum and a maximum relative counterion self-diffusion coefficient are observed for each of the four counterions. The value of  $D_r$  is the highest for the largest counterion (TBA<sup>+</sup>). The maximum  $D_r$  is found at higher polyion concentrations for the smaller counterions. At concentrations above the maximum,  $D_r$  decreases with increasing counterion radius, while at polyion concentrations below the maximum,  $D_r$  increases with increasing counterion radius. At the lowest polyion concentrations ( $c_p \approx 2 \times 10^{-3}$  monomol/(kg solution)) the dependence of  $D_r$  on the counterion radius has disappeared.

In figure 5(b) the calculated relative self-diffusion coefficients for four counterions of increasing radii in a spherical cell have been plotted as a function of concentration. The increasing radii of the counterions have been incorporated in the model by increasing the hard-sphere radius ( $R_s = 10, 11, 12, 13$  Å,  $N_q = 18$ ). The dependences on the polyion concentration and on the counterion radius are qualitatively well predicted over the entire polyion concentration range. Note that the value of  $D_r$  at the maximum depends on the radius as was also observed experimentally. With the PBS model for the cylindrical cell, this dependence is not found [1]. If the experimental data are corrected for the viscosity of the solvent, quantitative agreement of the model with experiment is found over a concentration



**Figure 5.** (a) The relative self-diffusion coefficient,  $D_r$ , of the TAA<sup>+</sup> ions in salt-free solutions of PMA in D<sub>2</sub>O against the logarithm of the PMA concentration,  $\log(c_p)$ . The PMA was neutralized to a degree of neutralization of 0.8.  $\square$ : TMA<sup>+</sup>;  $\blacktriangledown$ : TEA<sup>+</sup>;  $\diamond$ : TPA<sup>+</sup>;  $\bullet$ : TBA<sup>+</sup>. (b) The relative self-diffusion coefficient,  $D_r$ , as calculated using the PBS model for spherical symmetry ( $N_q = 18$ ; full curve:  $R_s = 1$  nm; dashed curve:  $R_s = 1.1$  nm; dashed-dotted curve:  $R_s = 1.2$  nm; dashed-double-dotted curve:  $R_s = 1.3$  nm). (c) The relative self-diffusion coefficient,  $D_r$ , of the TAA<sup>+</sup> ions, corrected for the self-diffusion coefficient for the solvent, for salt-free solutions of PMA in D<sub>2</sub>O, against the logarithm of the PMA concentration,  $\log(c_p)$ . The PMA was neutralized to a degree of neutralization of 0.8.  $\square$ : TMA<sup>+</sup>;  $\blacktriangledown$ : TEA<sup>+</sup>;  $\diamond$ : TPA<sup>+</sup>;  $\bullet$ : TBA<sup>+</sup>, together with the calculated values ( $N_q = 18$ ; full curve:  $R_s = 1$  nm; dashed curve:  $R_s = 1.1$  nm; dashed-dotted curve:  $R_s = 1.2$  nm; dashed-double-dotted curve:  $R_s = 1.3$  nm).

range from  $c_p \approx 0.01$  mol kg<sup>-1</sup> to  $c_p \approx 0.2$  mol kg<sup>-1</sup> (figure 5(c)).

Surprisingly enough, the counterion self-diffusion is much better described by the diffusion of a point charge around a charged sphere than by that around a charged cylinder. A polyion is by no means a hard sphere and a polyion solution is most certainly not a dispersion of non-interacting hard spheres, each containing a fraction of the total polyion charge. However, the ratio of the persistence length and the Debye screening length for salt-free solutions of vinylic polyions is of order unity at low polyion concentrations ( $c_p < 0.01$  monomol l<sup>-1</sup>), so at these concentrations the counterions are not cylindrically symmetrically distributed around the polyelectrolyte and the electric field experienced by the counterions can apparently be represented by the electric field of a charged sphere. Due to the flexibility of the vinylic chain and the interactions of the chain with the solvent, a counterion is on average under the influence of approximately 20 charges on the chain; the electric field set up by these charges can be approximated as possessing spherical symmetry.

At high concentrations the persistence length of the polyion is much larger than the Debye

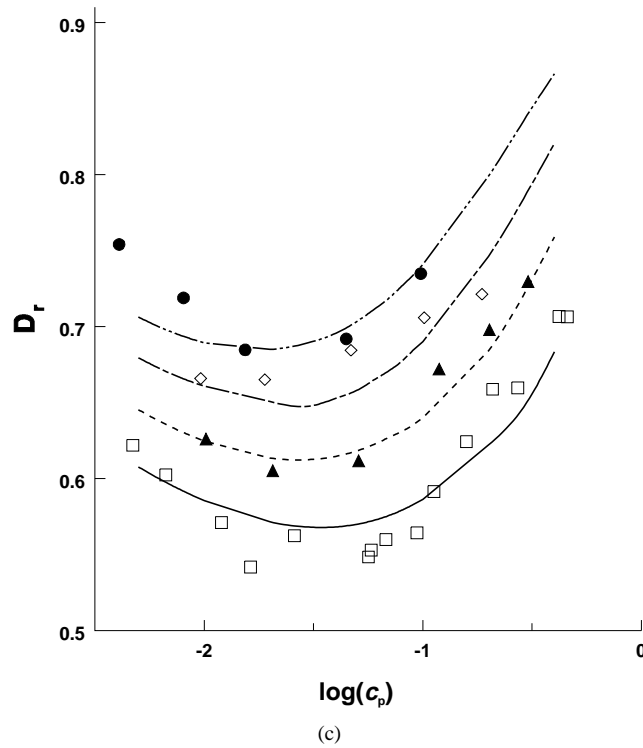
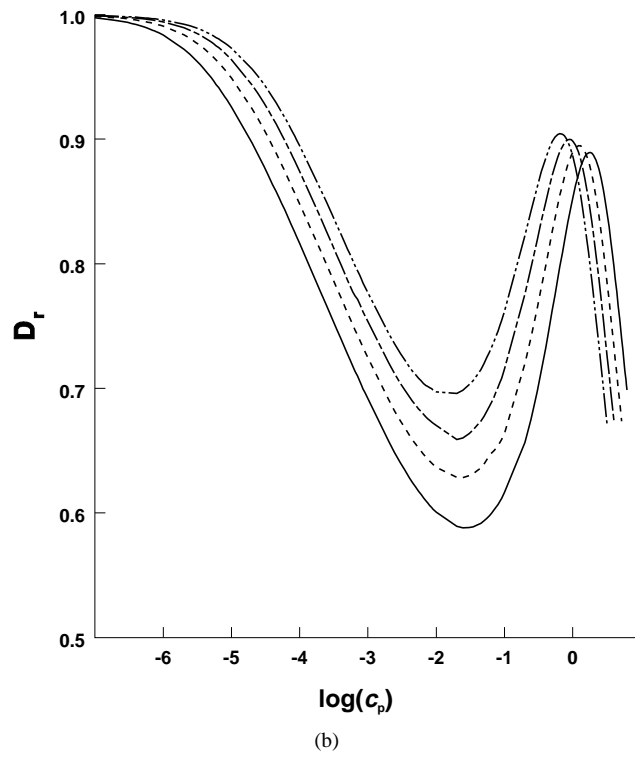


Figure 5. (Continued)

screening length, so the assumption that the polyion is cylindrically symmetrical becomes closer to reality. However, at high polyelectrolyte concentrations the average distance of the counterions from the polyion is small and the particular choice of the geometry of the polyelectrolyte is less important for the description of counterion dynamics.

#### 4. Conclusions

A low-, an intermediate- and a high-concentration regime exist for the concentration dependence of both the relative counterion self-diffusion coefficient and the self-diffusion coefficient of the polyion. In the low-concentration region,  $c_p < 0.01 \text{ mol kg}^{-1}$ , which coincides with the dilute polyion concentration regime, the polyion self-diffusion coefficient reaches the limiting value of the freely diffusing rod upon dilution. At concentrations above  $c_p \approx 0.1 \text{ mol kg}^{-1}$ , the self-diffusion coefficients of the counterion, the polyion and the solvent decrease upon concentration, reminiscent of a topological constraint on the motions of the constituents. Since the onset concentration of the decrease of  $D_p$  is slightly dependent on the molecular weight, and chain entanglement is thus unlikely, we propose that the concentration independence of  $D_p$  in the intermediate region is due to the combination of growing electrostatic interactions between the chains and decreasing chain dimensions. This is supported by the good description of the polyion self-diffusion coefficient at intermediate and high concentrations, by the diffusion of a hard sphere ( $R_{HS} = 3.7 \text{ nm}$ ) in a hard-sphere suspension, suggesting a sphere-like conformation of the polyion. The calculated obstruction effect of these hard spheres on the solvent reproduces the experimental solvent self-diffusion coefficients over the entire concentration range.

By making an appropriate choice of the sphere radius and the number of charges on the sphere, but at a surface charge density approximately equal to that used for the cylindrical model, the relative counterion self-diffusion coefficient calculated using the PBS model for the spherical cell agrees almost quantitatively with the experimental counterion self-diffusion coefficient, provided that a correction is made for the solvent viscosity. The number of charges on the sphere was of the order of the number of charges on a part of the chain about as long as the persistence length of the chain.

#### Appendix. The PBS model for the spherical cell [23]

An electro-neutral spherical cell of radius  $R_{\text{cell}}$  has one charged hard sphere of radius  $R_s$  at its centre, with a charge density defined by the number of charges,  $N_q$ . Immersed in the dielectric continuum surrounding the charged sphere are the monovalent counterions, with a charge opposite to that of the sphere, and possible additional electrolyte. The counterions and the additional electrolyte are treated as point charges. They are distributed in the Poisson–Boltzmann (PB) potential of the charged sphere in the spherical cell. In terms of the reduced electrostatic potential ( $\varphi = e\psi/(kT)$ ) the PB equation reads

$$-\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\varphi}{dr} \right) = \frac{e^2}{\varepsilon_0 \varepsilon_r kT} \sum_i n_i z_i \exp(-z_i \varphi) \quad (\text{A.1})$$

where  $r$  denotes the distance from the centre of the spherical cell. On putting  $\psi \rightarrow \infty$  for  $r < R_s$  the sphere becomes impenetrable for all ions. By adjustment of  $R_s$ , the effect of a counterion radius is introduced. Equation (1) was solved numerically under the boundary conditions  $\varphi(R_{\text{cell}}) = 0$  and  $\varphi'(R_{\text{cell}}) = 0$  (the prime denotes the derivative with respect to  $r$ ).

For monovalent counterions an expression for the relative self-diffusion coefficient,  $D_r$ , can be derived by solving the Smoluchowski equation, subject to the PB potential:

$$D_r = \chi(R_{\text{cell}}) \frac{n(R_{\text{cell}})}{n_{\text{avg}}}. \quad (\text{A.2})$$

Here,  $n(R_{\text{cell}})$  is the number concentration of counterions at the outer cell boundary,  $n_{\text{avg}}$  is the average number concentration of counterions in the spherical cell, which is just the stoichiometric concentration, and  $\chi(R_{\text{cell}})$  is determined by the first-order differential equation

$$r\chi' + \chi(1 + \chi - r\phi') - 2 = 0 \quad (\text{A.3})$$

under the boundary condition  $\chi(R_s) = 0$ .

## References

- [1] Schipper F J M, Hollander J G and Leyte J C 1997 *J. Phys.: Condens. Matter* **9** 11 179
- [2] Schipper F J M, Hollander J G and Leyte J C 1998 *J. Phys.: Condens. Matter* **10** 9207
- [3] Odijk T 1979 *Macromolecules* **12** 688
- [4] de Gennes P G, Pincus P, Velasco R M and Brochard F 1976 *J. Physique* **37** 1461
- [5] Dobrynin A V, Colby R H and Rubinstein M 1995 *Macromolecules* **28** 1859
- [6] Wijmenga S S, Van der Touw F and Mandel M 1985 *Physical Optics of Dynamic Phenomena and Processes in Macromolecular Systems* ed B Sedlack (Berlin: de Gruyter) p 87
- [7] Förster S, Schmidt M and Antonietti M 1990 *Polymer* **31** 781
- [8] Tanner J E 1970 *J. Chem. Phys.* **52** 2523
- [9] Stejskal E O 1965 *J. Chem. Phys.* **43** 3597
- [10] Tanahatoe J J and Kuil M 1997 *J. Phys. Chem. B* **101** 10 839
- [11] Walkenhorst, R, Dorfmueller Th and Eimer W 1995 *Ber. Bunsenges. Phys. Chem.* **99** 1137
- [12] Doi M and Edwards S F 1988 *The Theory of Polymer Dynamics* (Oxford: Clarendon)
- [13] Aver H E and Alexandrowitz Z 1969 *Biopolymers* **8** 1
- [14] Kassapidou K, Jesse W, Kuil M E, Lapp A, Egelhaaf S and Van der Maarel J R C 1997 *Macromolecules* **30** 2671
- [15] Koene R S and Mandel M 1983 *Macromolecules* **16** 973
- [16] Oostwal M G, Blees M H and De Bleijser J 1993 *Macromolecules* **26** 7300
- [17] Tanahatoe J J and Kuil M 1997 *J. Phys. Chem. B* **101** 9293
- [18] Kaji K, Urakawa H, Kanaya T and Kitamaru R 1988 *J. Physique* **49** 993
- [19] Nishida K, Urakawa H, Kaji K, Gabrys B and Higgins J S 1997 *Polymer* **38** 6083
- [20] Cichocki B and Hinsen K 1990 *Ber. Bunsenges. Phys. Chem.* **94** 243
- [21] Boué F, Cotton J P and Jannink G 1994 *J. Chem. Phys.* **101** 2562
- [22] Jönsson B, Wennerström H, Nilsson P G and Linse P 1988 *Colloid Polym. Sci.* **264** 77
- [23] Bell G M 1964 *Trans. Faraday Soc.* **60** 1752
- [24] Schipper F J M, Kassapidou K and Leyte J C 1996 *J. Phys.: Condens. Matter* **8** 9301
- [25] Ander A and Lubas W 1981 *Macromolecules* **14** 1058
- [26] Rymdén R and Stilbs P 1985 *J. Phys. Chem.* **89** 3502
- [27] Woodbury C P and Ramanathan G V 1982 *Macromolecules* **15** 82
- [28] Yoshida N 1978 *J. Chem. Phys.* **69** 4867
- [29] Nilsson L G, Nordenskiöld L, Stilbs P and Braunlin W H 1985 *J. Phys. Chem.* **89** 3385
- [30] Boué, F, Cotton J P, Lapp A and Jannink G J 1994 *J. Chem. Phys.* **101** 2562
- [31] Spiteri M N, Boué F, Lapp A and Cotton J P 1996 *Phys. Rev. Lett.* **77** 5218
- [32] Borochoy N and Eisenberg H 1994 *Macromolecules* **27** 1440
- [33] Finney J L and Turner J 1988 *Faraday Discuss. Chem. Soc* **85** 125