

Ionic Transport in Polyelectrolyte Gels: Model and NMR Investigations

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ABSTRACT: The diffusion of ions in polyelectrolyte gels has been investigated both theoretically and experimentally. A simple phenomenological model was first developed, building upon the geometric obstruction theory developed originally for the diffusion of neutral and charged species in neutral gels. The electrostatic obstruction is accounted for by (a) adopting an effective chain diameter obtained from the Dobrynin scaling theory for polyelectrolytes and (b) adding an exclusion layer of thickness $\delta(c_s)$ around the charged chains to describe the electrostatic interaction between the ions and the chains. Then the diffusion of water and organic ions in an organically cross-linked polyacrylamide gel was studied experimentally using nuclear magnetic resonance (NMR). The relative diffusion coefficients $D_r = D_g/D_0$ (D_g = diffusion in gel, D_0 = diffusion in solvent) of the different species were measured for various polymer, cross-linker, and salt concentrations. The calculated predictions and the measured data were found to be in good agreement. For water molecules, we obtain $D_r = 0.92 \pm 0.01$ independently of salt content, which is consistent with a pure geometric obstruction. For monovalent anions and cations (butyrate, Bu^- , and tetramethylammonium, TMA^+) D_r increases from about 0.5 to 0.75 when the ion concentration increases from 0 to 150 mol/m³. For the divalent cation (putrescine, Pu^{2+}) the D_r are generally higher and increase from 0.6 to about 0.92, indicating an almost complete elimination of the electrostatic obstruction, consistent with a more efficient screening of the charges in the chains.

Introduction

It is well established that the thermal motion of small solute species is considerably hindered in hydrophilic gels, giving rise, on the macroscopic level, to a strong reduction in the diffusion coefficients of the solute species. This phenomenon forms the basis for a large number of applications, including controlled drug delivery,¹ gel permeation chromatography,² various wastewater treatment processes,³ and subsoil environmental applications.^{4,5} Owing largely to the development of these applications, the diffusion of small molecules in hydrophilic gels has been the subject of numerous studies in the past few decades.^{6–8}

The phenomenological theories emerging from those studies can be classified in three main categories. (a) The free volume theories⁶ extend the hole-hopping concept, originally developed for solute diffusion in pure liquids, to polymeric systems. (b) The hydrodynamic theories⁷ assume that the polymer chains enhance the frictional drag on the solute by slowing down fluid flow near the chains. (c) Finally, the obstruction theories are based on the idea that the presence of impenetrable polymer chains causes an increase in the effective path length for diffusive transport. Recently, Amsden⁸ compared several theories belonging to the above three categories and concluded that, for homogeneous hydrogels composed of flexible polymer molecules, the obstruction theories provide the best fit to the available experimental data. Hence, in this work we shall adopt the obstruction approach.

The models described above were developed for the diffusion of neutral or charged solutes (ions) in neutral

gels and describe essentially a purely geometric obstruction. In cases where charged species diffuse through polyelectrolyte gels (i.e., gels obtained by cross-linking charged polymer molecules), however, the electrostatic interaction between the diffusing species and the charged chains give rise to an additional obstruction, which we shall characterize as an electrostatic obstruction. The purpose of this paper is therefore to provide a quantitative analysis of diffusion of ions in polyelectrolyte gels taking into account this electrostatic obstruction, in addition to the geometric obstruction. First, a simple phenomenological model will be presented. The model is based on the premise that, while moving through the gel, the solute encounters a series of openings between the polymer chains, having a varying diameter. The electrostatic obstruction effects are taken into account by introducing an effective chain radius comprising two contributions: (a) the electrostatic chain radius proper and (b) an increment of this radius due to electrostatic interaction between the ions and the polymer chains. Second, an experimental study of the diffusion of mono- and divalent cations and monovalent anions in an organic gel conducted using the nuclear magnetic resonance (NMR) technique will be presented. The gel was obtained by cross-linking partially hydrolyzed polyacrylamide (HPAM) with glyoxal (HCOCHO). Self-diffusion coefficients were measured as a function of the physical parameters, i.e., the concentrations of polymer, cross-linker, and salt. The experimental data are compared with the calculated predictions, and then we draw the main conclusions of this study.

Theoretical Section

Diffusion in Pure Solvent. For simplicity, we represent the diffusing species (water molecules, ions, etc.) by spheres with hydrodynamic radius r_s . In a pure

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Table 1. Values Used in Calculations for Different Parameters

<i>b</i> (Å)	<i>A</i>	<i>U</i>	<i>r_s</i> (Å)		
			TMA	Pu	Na butyrate
2.5 ⁸	3	3	3.5 ^a	3 ^a	4.7 ^a

^a Calculated from eq 1 at 25 °C.

solvent the diffusion coefficient D_0 is given by the Stokes–Einstein equation

$$D_0 = \frac{k_B T}{4\pi\eta r_s} \quad (1)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η the viscosity of the solvent (deuterated water D₂O) at the operating temperature. The term 4 in the denominator of eq 1 is a geometric correction factor. The hydrodynamic radius of the ions can thus be estimated from the diffusion coefficients measured during the NMR experiments using eq 1. The values of the parameters used in this work are given in Table 1. The remainder of this analysis addresses the question of how the diffusion coefficient given by eq 1 is modified in the presence of a polyelectrolyte gel.

Gel Physical Model. In the polyacrylamide gels similar to the one considered in this study, the chains form a disordered three-dimensional network with the space between the polymer molecules entirely occupied by the solvent. However, to simplify the formulation of the theory, we shall adopt an idealized picture where the polymer chains in the gel form a square lattice and the cross-links are tetrafunctional.⁹ The network will mainly be characterized by an average opening radius R . This quantity can be estimated from scaling concepts for polyelectrolytes, using the principle introduced by De Gennes,¹⁰ that the gel state is equivalent to the semidilute solution at the overlap concentration. The conformation of a chain in the network is considered to be rodlike; i.e., the chain is a fully extended assembly of electrostatic blobs. The Coulomb repulsion inside each blob is not sufficient to deform the chain. Thus, the effective chain radius r_f^e is approximately equal to the sum of the electrostatic blob radius r_f and the thickness of the electrostatic exclusion layer δ , that is, $r_f^e = r_f + \delta$.

Network Opening and Chain Diameter. To determine R and r_f , we use results of the theory of Dobrynin et al.¹¹ for polyelectrolytes. Suppose that we have a semidilute solution of semiflexible polyelectrolyte chains in good solvent conditions and under essentially salt-free conditions (i.e., no salt added). Then, according to Dobrynin, the correlation length ξ_{ns} scales like

$$\xi_{ns} \simeq \left(\frac{B}{cb}\right)^{1/2}; \quad B \simeq \left(\frac{A^2}{u}\right)^{2/7} \quad (2)$$

where c is the polymer concentration, b the monomer length, A the number of monomers between effective charges, and $u = l_B/b$, where l_B is the Bjerrum length. Moreover, we assume that r_f is equal to the electrostatic blob radius; therefore, r_f scales like

$$r_f \simeq \frac{b}{2} \left(\frac{A^2}{u}\right)^{3/7} \quad (3)$$

Note that eqs 2 and 3 are based on the assumption that

Table 2. Regression Results for Diffusion of TMA, Pu, and Na Butyrate

solute	k_s	k_s'	r_f (Å) ^a
TMA ⁺	1.53 ± 0.10	1.59 ± 0.11	3.17 ± 0.22
Pu ²⁺	1.88 ± 0.13	2.01 ± 0.14	4.02 ± 0.28
butyrate [−]	1.73 ± 0.12	1.83 ± 0.13	3.66 ± 0.26

^a The sensitivity calculations for the error in this value was found to be negligible.²³

the electrostatic persistence length is much larger than the intrinsic persistence length.

Exclusion Layer. To capture the additional hindrance of ion diffusion due to electrostatic interaction between the ions and the charged chains in the gel, we introduce an effective exclusion zone around the chains, in agreement with an earlier work of Stigter.¹² The thickness of the exclusion layer $\delta(c_s)$ depends on salt concentration and can be calculated by solving the Poisson–Boltzmann (PB) equation for the electrostatic potential around the polymer chain. The cylindrical cell model is used to carry out this computation numerically for the following boundary conditions: (a) the potential gradient at the surface of the chain (i.e., at $r = r_f$) equals the charge density, and (b) the potential gradient at a distance $r = r_c$ (r_c is the solvent cylinder radius around the chain assuming equal cylinders around the chains) equals zero. The parameters used for PB solution are as follows: r_f values are shown in Table 2 and $r_c = 12.73$ Å. As a first approximation, $\delta(c_s)$ is chosen to be the distance at which the electrostatic potential equals the thermal energy $k_B T$.

Geometric Obstruction. Returning to the diffusion of ions in gels, first we recall the obstruction-scaling model of Amsden⁹ for the diffusion of neutral and charged species in homogeneous neutral gels. Our aim is to modify this model to incorporate the electrostatic obstruction effects. In the context of the obstruction-scaling theory, the relative diffusion coefficient, $D_r = D_g/D_0$, where D_g is the diffusion coefficient of the solute in the gel, can be expressed by

$$D_r = \frac{D_g}{D_0} = \exp\left[-\frac{\pi}{4}\left(\frac{r_s + r_f}{R}\right)^2\right] \quad (4)$$

where r_s is the radius of the diffusing solute molecule; r_f and R are as defined above. The sum $r_s + r_f$ represents the critical limiting radius required to permit solute passage. The exponential form of eq 4, on the other hand, describes the statistical origin of D_g and can be explained as follows. While moving through the network, the ions encounter a series of openings between the chains whose diameter is larger than their own diameter: eq 4 derives from the probability of encountering such openings. This equation is valid for the polyacrylamide gels used in this study, as these gels have been proved to be fairly homogeneous.¹³

Electrostatic Obstruction. To obtain the relative self-diffusion coefficient for ions in a polyelectrolyte gels, we modify eq 4 in two ways. (a) Extending the De Gennes principle of correspondence between the gel state and semidilute sol to polyelectrolytes, we take the average radius of the gel network opening R to be equal to half of the correlation length ξ_{ns} for the semidilute polyelectrolyte solution, i.e., $R = \xi_{ns}/2$. This is slightly different from what Amsden did because we choose the correlation length to be measured between the centerline of the chains and not between the chains faces. This

choice is in line with the scaling theory by De Gennes that was developed for chains with negligible thickness and with the choice of the second moment of the distribution of mass which is by definition related to the center of mass while measuring the correlation length using neutron or X-ray scattering (b) For the chain diameter, we take the sum of the polyelectrolyte chain diameter r_f , given by eq 3, and the thickness of the exclusion layer around the chain $\delta(c_s)$; i.e., the effective chain radius is $r_f^e = r_f + \delta(c_s)$. Consequently, eq 4 becomes

$$D_r = \exp \left[-\pi \left(\frac{r_s + r_f^e}{\xi_{ns}} \right)^2 \right] \quad (5)$$

Recall that ξ_{ns} is the correlation length for the case of no salt added. Substituting eqs 2 and 3 in eq 5, we can express the relative diffusion coefficient for ions (cations and anions) in polyelectrolyte gels $D_r(c_s)$ as

$$D_r(c_s) = \exp[-\pi(F(c_s))^2] \quad (6)$$

with

$$F(c_s) = \frac{r_s + \delta(c_s) + K_s \frac{b(A^2)}{2u}^{3/7}}{k_s \left(\frac{B}{cb} \right)^{1/2}} \quad (7)$$

where k_s and K_s are the scaling constants for the correlation length ξ_{ns} and the effective chain radius r_f^e , respectively. These coefficients are specific to the polymer-solvent system. From the model it is clear that at excess added salt $\delta(c_s)$ will be negligible, and the geometric obstruction will be dominant. Note finally that the dependence on salt concentration due to ξ_{ns} and r_f was ignored because, under the experimental conditions of this study, these two parameters are weakly dependent on salt concentration.

Experimental Section

Materials. Partially hydrolyzed polyacrylamide with 25% degree of hydrolysis and molecular weight of 100 000 Da was used at a concentration of 20% active material dissolved in water to form a polymer solution from SNF-Floerger. Glyoxal with 40% concentration in water was used as a cross-linker. The HPAM-glyoxal gel is rubbery when freshly prepared but becomes glassy upon drying and floppy upon swelling in the presence of water. When left to swell freely, the gel can absorb large amounts of water. The HPAM-glyoxal gel was chosen for this study because of its potential for environmental applications.^{14,15}

Three organic salts were used to conduct the experiments: (a) tetramethylammonium chloride $\text{TMACl}[(\text{CH}_3)_4\text{NCl}]$ as a monovalent salt, (b) putrescine dichloride $\text{PuCl}_2[\text{NH}_3(\text{CH}_2)_2\text{NH}_3\text{Cl}_2]$ as a divalent salt, and (c) sodium butyrate $[\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{Na}]$ as a monovalent salt.

Samples Preparation. Because of the small difference in the chemical shift between the protons in water and in ions, the polymer solution and the cross-linker were freeze-dried and dissolved in D_2O to enable the separation of the signals corresponding to the ion and water protons during NMR spectroscopy. Moreover, salt solutions were all prepared in D_2O . To prepare gel samples, different amounts of cross-linker (2.5–15.0%) and D_2O of (47.5–35.0%) were added to 50 vol % of polymer solution in D_2O while stirring until homogeneous solutions were obtained. Then the solution was put in the 5 mm NMR tubes to a height of 4 mm, and the tubes were sealed to prevent the loss of volatile components. Subsequently, the

NMR tubes were heated for 7 h at 50 °C to let gelation take place. Thus, the gelation took place under the no salt added condition. After gelation, the tubes were let to cool to room temperature, and then salt solutions in D_2O with different concentrations were added to the gel, in the NMR tubes, to a height of 8 mm. Then, the gel and the salt solutions were left to equilibrate to obtain a homogeneous sample with 8 mm total height to ensure gradient homogeneity over the entire sample volume. Thus, the salt solution constituents diffused inside the gel leading to swelling, according to Flory's¹⁶ affine network theory of rubber elasticity, in the direction parallel to the axis of the tube (diffusion direction) and to the development of swelling pressure in the perpendicular direction to the axis of the tube. The latter is due to the hindrance of swelling perpendicularly to the walls of the NMR tubes. The longitudinal and transverse relaxation rates of the ions were approximately equal; thus, the conventional pulsed field gradient method was used. To make sure that the values are reproducible and to avoid the time dependence of the NMR measurements, the measurements were repeated after certain times to ascertain whether there were any changes in the measured values. The diffusion coefficients were unchanged upon prolonged storage.

NMR Spectroscopy Procedure. Hydrogen pulsed field gradient nuclear magnetic resonance (H-PFG-NMR) experiments were conducted to measure the self-diffusion coefficients.

The self-diffusion coefficients of the tetramethylammonium and putrescine cations as well as the butyrate anion were measured by the stimulated echo modification of the pulsed field gradient method.¹⁷ These experiments were carried out on a Bruker AM200 spectrometer, equipped with a 4.7 T wide bore superconducting magnet. A maximum magnetic field gradient, $G = 0.5$ T/m, along the direction of the main magnetic field was generated by an actively shielded gradient coil with a Techtron 7570 amplifier. The gradient pulses are characterized by rise and fall times on the order of 0.1 ms, the duration of the gradient pulses d was 2 ms, and the waiting period between pulses Δ was always 20 ms. Prior to the application of the second rf pulse or signal accumulation, the gradient pulse was followed by a 20 ms delay to allow for relaxation of eddy currents. Thirty-two free induction decays (FIDs) were collected in which the pulsed field gradient intensity was incremented. After Fourier transformation of the FIDs, the integral of the small ion proton resonance $A(G)$ was integrated and fitted to

$$A(G) = A_0 \exp \left[-\gamma^2 G^2 \left(\Delta - \frac{1}{3}d \right) D \right]$$

with A_0 the integral at zero gradient, γ the gyromagnetic ratio of the proton, and D the self-diffusion coefficient. All measurements were done at 25 °C.

Three sets of H-PFG-NMR experiments were conducted to measure the self-diffusion coefficients. The first set of experiments was aimed at measuring the diffusion coefficient of the monovalent organic cations and water in the gel for several salt and cross-linker concentrations. The cross-linker concentration was changed from 2.5 to 15 vol % to study its effect on the measured self-diffusion values. To check the validity of the assumption that ξ_{ns} and consequently r_f are weakly dependent on salt concentration, due to the experimental conditions, the water relative self-diffusion coefficient was measured for different salt concentrations. To study the influence of the valence of the diffusing salt, a second set of experiments was performed to determine the diffusion coefficient of the divalent organic cations and water in the gel at different salt concentrations. The third set was carried out to measure the diffusion coefficient of the monovalent organic anion in the gel at different salt concentrations.

Results and Discussion

Gel Characterization. To characterize the gel system and calibrate the NMR system, proton spectra were

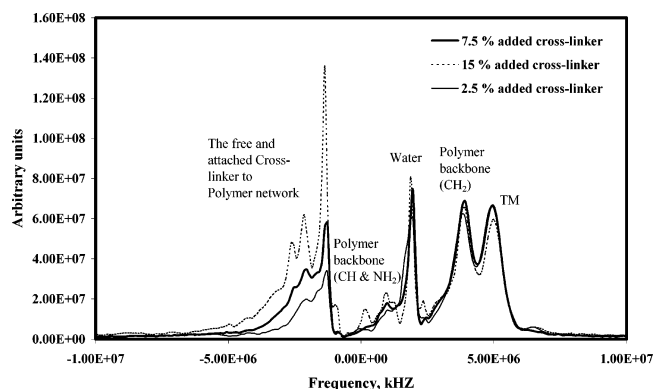


Figure 1. ^1H spectrum obtained from Fourier transformation of the stimulated echo in PFG self-diffusion experiment. A number of peaks or groups of peaks can be seen.

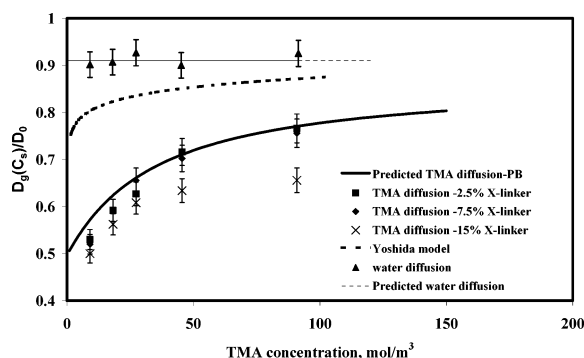


Figure 2. Measured (points) and fitted relative self-diffusion coefficient ($D_r(c_s)$) of the monovalent cations (TMA), using Yoshida's model (dotted line) and eq 6 (line), with different percentage of cross-linker added, and that measured for water (triangles) and fitted (dashed line), using eq 6, with 7.5% cross-linker added, vs the TMA concentration.

obtained during the NMR measurements for TMA and water diffusion at different cross-linker concentrations. The spectra are grouped in Figure 1. From low to high frequencies we can distinguish five peaks or group of peaks: (a) free cross-linker peaks (narrow peaks) and cross-linker attached to the polymer chains (broad peaks), (b) backbone peaks (CH, NH_2 , etc.), (c) the water peak and (d) the backbone peak (CH_2), and finally (e) the peak of the TMA. The following observations can be made concerning the peaks corresponding to the cross-linker. First of all we note that the integral of the surface under the peaks matches well with the nominal concentration of the cross-linker, which proves the consistency of the experiments. Furthermore, the ratio of free-to-bound cross-linker increases considerably with increasing cross-linker concentration, suggesting that an optimal cross-linker concentration exists: above this concentration, a large amount of free cross-linker molecules will be present in the gel.

Water Diffusion. One of the consequences of obstruction theory is that the geometrical obstruction should be dependent on salt concentration, as the latter induces changes in the average opening of the gel network. This was tested and found in agreement by measurements of the relative self-diffusion of (neutral) water molecules at various salt concentrations. Recall that the relative diffusion is the ratio between the self-diffusion coefficients in the gel and the solvent (D_2O in this case). The data are shown in Figure 2. The calculated value (horizontal line) obtained from eq 5 and the experimental value $D_r = 0.92 \pm 0.01$ (triangles) are

in good agreement. The data show furthermore that the relative water self-diffusion coefficient is independent of the salt concentration. This indicates that the average opening of the polymer network and consequently r_f , perpendicular to the diffusion direction, are essentially constant for the range of the salt concentrations investigated. The little sensitivity of the opening of the gel network can be attributed to two opposing effects: (a) The first is the swelling of the network due to the diffusion of D_2O into the gel body. However, this swelling of D_2O is hindered by the confinement of the gel within the walls of the NMR tube in the direction perpendicular to the diffusion direction, which results in the development of a swelling pressure. (b) The second effect is the shrinkage of the chains due to the screening of their charges by the ions resulting from the dissociation of the salt. Apparently these two effects cancel mutually. A plausible alternative explanation for the independency of the water diffusion on the salt concentration is that due to the relatively large difference between the size of the water molecule and the average network opening. Thus, the water molecule experiences no hindered diffusion.

Monovalent Cation Diffusion. Now we turn to the diffusion of ions in the gel. Figure 2 also shows the relative self-diffusion coefficient D_r for the TMA (organic) monovalent cations measured using the NMR spectroscopy technique fitted using our model as a function of concentrations of TMA. Note that changes in the concentration of TMA amount also to changes in ionic strength in the gel. The ratio between the relative self-diffusion coefficient for the ions in gel and in water increases with salt concentration and seems to tend to a plateau. The same trend was observed previously by several workers^{18,19} who found also that the gel diffusivity decreases as the flexibility of the polymer backbone decreases. The values of D_r , calculated using the solution of the PB equation to determine the effective chain thickness, agree well with the measured ones for 2.5–7.5% added cross-linker. For the gel containing 15% cross-linker, the measured D_r values are considerably lower than for the gels with lower cross-linker content. The reason for this behavior is not completely clear. However, the NMR spectra for the cross-linker suggest that it might be attributed to the presence of free cross-linker, which is not contributing to the network: possibly the excess cross-linker affects the network average opening. In the spectra, a peak was found that increases with the increase of the added cross-linker and disappeared for concentrations lower than 7.5 vol %. This indicates that for added cross-linker up to 7.5 vol % there was only a small amount of free cross-linker in the gel.

On the other hand, our results were compared with those calculated using Yoshida's theory.²⁰ This theory was developed to calculate the ion diffusion coefficient in polyelectrolyte solutions based on the cell model with cylindrical symmetry. It contains some of the important features although it was not developed for gels. The trends of our calculated and experimental curves are again in good agreement with Yoshida's theory, but Yoshida's data are shifted upward. This shift can be attributed to the fact that Yoshida's theory assumes unconstrained diffusion along the chain, in contrast with the theories of Manning²¹ and Rymden.²² Moreover, the shift is larger at lower salt concentrations (strong potential) than at higher salt concentrations (weak

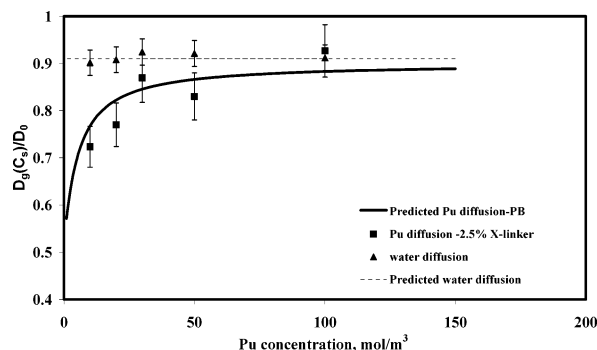


Figure 3. Measured (squares) and fitted (line) relative self-diffusion coefficient ($D_r(C_s)$) of the divalent cations, Pu, with 7.5% added cross-linker, and that measured for water (triangles) and fitted (dashed line), using eq 6, vs the Pu concentration.

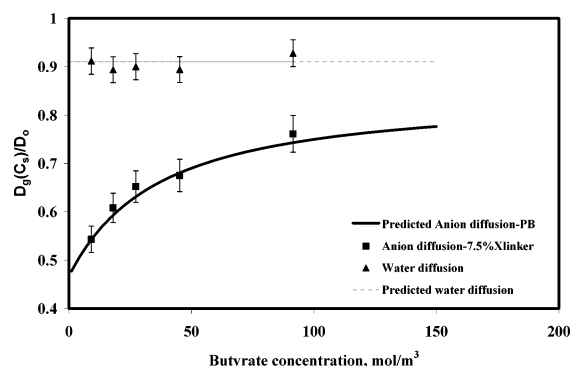


Figure 4. Measured (points) and fitted (line) relative self-diffusion coefficient ($D_r(C_s)$) of the monovalent anions with 7.5% added cross-linker, and that measured for water (triangles) and fitted (dashed line), using eq 6, vs the Butyrate concentration.

potential). This is because Yoshida's model is based on the Debye–Hückel approximation solution for the PB equation, which performs well for weak potentials.

Divalent Cation Diffusion. Figure 3 gives the relative diffusion coefficient fitted and measured for the organic divalent cation Pu at different Pu concentrations. The calculated curve and the experimental data are in fairly good agreement. Comparing Figures 2 and 3, we observe that the relative diffusion coefficients for the divalent counterions are higher than for the monovalent counterions in the interval of salt concentrations investigated. This shows that the divalent counterions are much more efficient in balancing the electrostatic obstruction effects. The increase of D_r with the salt concentration is larger in the presence of 2:1 salt than for 1:1 salt, for both calculated and measured self-diffusion coefficients in good agreement with previously published data.¹⁹ Figure 3 shows the measured and the fitted relative water self-diffusion coefficient as well. The measured and fitted values are in a good agreement and shown to be independent of the salt concentration, which means that the average opening of the polymer network and consequently r_f , perpendicular to the diffusion direction, are constant for the range of the salt concentrations used.

Monovalent Anion Diffusion. Figure 4 shows the relative diffusion coefficients fitted by our model and those obtained with the NMR technique for the organic monovalent anions at different concentrations of the diffusing species. The fitted and measured data are again in rather good agreement, which supports the

validity of the proposed model for the diffusion of both anions and cations in polyelectrolyte gels. Likewise for Figure 3, Figure 4 shows the measured and the fitted relative water self-diffusion coefficient as well. The measured and fitted values are in a good agreement and shown to be independent of the salt concentration, which means that the average opening of the polymer network perpendicular to the diffusion direction and consequently r_f are constant for the range of the salt concentrations used. The geometrical obstruction for the ions could be calculated in the same way as that for water molecules; thus, the contribution of the electrostatic obstruction could be distinguished from the total obstruction. Indeed, the electrostatic obstruction is considerable at low salt concentrations and decreases with the increase of salt concentration due to the screening of the charges on the polymer network.

k_s and k_s' were estimated by fitting eq 6 to the three NMR data sets. The curve fitting was done using Curve Expert software, which employs the Levenberg–Marquardt nonlinear regression algorithm. The regression was done by trial and error as follows. First, an initial trial value is assumed for r_f^e . Then the corresponding values for k_s and k_s' are determined. The value of k_s' obtained in this way is then used to compute r_f^e . This process is repeated with a new r_f^e trial value until the calculated value of r_f^e equals the trial one. The values of the constants k_s and k_s' obtained from the regression are listed in Table 2.

Conclusions

A phenomenological model for the diffusion of ions in polyelectrolyte gels was developed. In addition to the geometrical hindrance already taken into account in the existing models, our model includes the electrostatic hindrance of the diffusion process. The model predicts, among other things, that the relative self-diffusion coefficient for mono- and divalent cations and for anions should be much lower than that for neutral species such as water for instance. Hydrogen pulsed field gradient nuclear magnetic resonance (H-PFG-NMR) experiments confirmed that while the relative self-diffusion coefficient of water molecules is only 0.92, that of anions is at the lowest concentration of diffusing species a factor 2 lower. This supports the proposed model and shows the significance of electrostatic contribution to the hindrance of diffusion. This hindrance decreases however when the concentration of diffusing ions (i.e., the salinity) increases. In the limit of large salinity our results become closer to those of Amsden,²³ corresponding to an essentially geometric obstruction.

A final note about the limit of the validity of the proposed model is called for. Although the model was proved to agree well with the experimental results, it is only valid within the territory of acceptability of its assumptions. In the derivation of the model a number of assumptions have indeed been made, as was mentioned previously by Amsden:⁹ (1) Water is a good solvent for the polymer. (2) The polymer chain distance between cross-links is greater than the persistence length of the polymer; therefore, scaling concepts can be applied. (3) The conformation of the chain is considered to be a rodlike (i.e., fully extended) assembly of electrostatic blobs. (4) The polymer physical properties in the gel state are equivalent to its physical properties in the solution state.

The third assumption appears rather radical indeed since the polymer chains comprising the homogeneous gels used in this study are definitely not even close to a rodlike conformation. The use of a rodlike geometry is acceptable, however, as Chui et al.²⁴ used this picture rather successfully to estimate the pore radii distributions for polyacrylamide gels from NMR relaxation measurements as mentioned earlier by Amsden.⁹

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References and Notes

- (1) Ranter, B. D. Biomedical Applications of Synthetic Polymers. In *Comprehensive Polymer Science*; Aggarawl, S. L., Ed.; Pergamon Press: Toronto, 1989; Vol. 7, p 201.
- (2) Moussaoui, M.; Benylas, M.; Wahl, P. *J. Chromatogr., A* **1991**, *558*, 71–80.
- (3) Araujo, M. M.; Teixeira, J. A. *Int. Biodet. Biodeg.* **1997**, *40*, 63.
- (4) Yoshihito, O.; Kanji, K. *Gels Handbook*; Academic Press: San Diego, 2001; Vol. 4.
- (5) Apps, J. A.; Persoff, P.; Moridis, G.; Pruess, K. Method for formation of subsurface barriers using viscous colloids. United States Patent 5,836,390, Nov 1998.
- (6) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164.
- (7) Cukier, R. J. *Macromolecules* **1984**, *17*, 252.
- (8) Amsden, B. *Macromolecules* **1998**, *31*, 8382.
- (9) Amsden, B. *Macromolecules* **1999**, *32*, 874.
- (10) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
- (11) Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. *Macromolecules* **1995**, *28*, 1859.
- (12) Tanaka, T. *Sci. Am.* **1981**, *244*, 110.
- (13) Stigter, D. *Biopolymers*, **1977**, *16*, 1435.
- (14) Darwish, M. I. M.; van der Maarel, J. R. C.; Pel, L. H. H.; Zitha, P. L. J. Polymer Gel Barriers for Waste Disposal Facilities. In *Geotechnical Engineering: Meeting Society's Needs*; Ho, K. K. S., Li, K. S., Eds.; Balkema Publisher: Rotterdam, 2001; Vol. 1, pp 225–230.
- (15) Darwish, M. I. M.; van der Maarel, J. R. C.; Pel, L.; Huinink, H.; Zitha, P. L. J. Polymer gel Barriers for Contaminant Containment. In *Environmental Geotechnics*; de Mello, L. G., Almeida, M., Eds.; Balkema Publisher: Rotterdam, 2002; Vol. 1, pp 77–82.
- (16) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
- (17) Callaghan, P. T. *Principles of Nuclear Magnetic Resonance Microscopy*; Clarendon: Oxford, 1991.
- (18) Amsden, B. *Macromolecules* **2001**, *34*, 1430.
- (19) Schipper, F. J. M.; Hollander, J. G.; Leyte, J. C. *J. Phys.: Condens. Matter* **1998**, *10*, 9207.
- (20) Yoshida, N. *J. Chem. Phys.* **1980**, *72*, 1365.
- (21) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
- (22) Rymden, R.; Stilbs, P. *J. Phys. Chem.* **1985**, *89*, 2425.
- (23) Amsden, B.; Grotheer, K.; Angl, D. *Macromolecules* **2002**, *35*, 3179.
- (24) Chui, M. M.; Phillips, R. J.; McCarthy, M. J. *J. Colloid Interface Sci.* **1995**, *174*, 336.

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