

## NMR Water Self-Diffusion and Relaxation Studies on Sodium Polyacrylate Solutions and Gels in Physiologic Ionic Solutions

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**ABSTRACT:** Water self-diffusion coefficients and longitudinal relaxation rates in sodium polyacrylate solutions and gels were measured by NMR, as a function of polymer content and structure in a physiological concentration range of monovalent and divalent cations,  $\text{Ca}^{2+}$  and  $\text{Na}^+$ . Several physical models describing the self-diffusion of the solvent were applied and compared. A free-volume model was found to be in good agreement with the experimental results over a wide range of polymer concentrations. The longitudinal relaxation rate exhibited linear dependence on polymer concentration below a critical concentration and showed non-linear behavior at higher concentrations. Both the water self-diffusion and relaxation were less influenced by the polymer in the gel state than in the uncrosslinked polymer solutions. The effect of  $\text{Na}^+$  on the mobility of water molecules was practically undetectable. In contrast, addition of  $\text{Ca}^{2+}$  strongly increased the longitudinal relaxation rate while its effect on the self-diffusion coefficient was much less pronounced. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40001.

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### INTRODUCTION

Knowledge of the dynamics of small molecules in polymeric materials is important to advance polymer-based technologies such as membrane separations, barrier materials, controlled drug release, ion-exchangers, packaging, biosensors, and chemical sensors.<sup>1–3</sup> Polyelectrolyte hydrogels are environmentally sensitive (pH and counterions), and can be used for site-specific drug delivery.<sup>4,5</sup> Many anionic polyelectrolyte gels exhibit an abrupt volumetric phase transition in the presence of multivalent cations in the physiological concentration range.<sup>6,7</sup> This phenomenon is believed to underlie important physiological processes such as nerve excitation and muscle contraction.<sup>6–11</sup> Investigating the physical properties of synthetic polyelectrolyte gel model systems may lead to a better understanding of these phenomena. For these reasons, substantial work has been done to characterize the thermodynamic properties and structure of polyelectrolyte gels and the dynamics of small molecules in polymer matrices (e.g., concentrated solutions and gels).

It has been demonstrated that water plays an essential role in determining the physical properties of polyelectrolyte systems (e.g., solutions of RNA, DNA, and proteins).<sup>12,13</sup> Experimental

studies as well as simulations demonstrated a strong coupling between the dynamics of polymer and solvent molecules.<sup>14,15</sup> It has been reported that the dynamics of biomolecules is strongly coupled to the onset of translational motions of hydration water,<sup>16,17</sup> and the orientational dynamics of water molecules is changed by the polymer.<sup>18,19</sup> However, the mechanism of this coupling is poorly understood.

Previous studies have raised several important questions: Does the presence of the polyelectrolyte chain affect only the translational mobility of the water or does it also influence the orientational mobility? What is the molecular mechanism underlying these processes? Is the dynamics of water different in gels and in solutions of the same uncrosslinked polymer at the same polymer concentration? How does monovalent–divalent ion exchange affect the dynamics of water in polyelectrolyte systems? To address these questions, we determined the mobility of the solvent (water) in model sodium polyacrylate (NaPA) solutions and gels by NMR spectroscopy. The self-diffusion coefficient and longitudinal relaxation rate of water were measured as a function of the polymer concentration. Water self-diffusion is governed by its local translational mobility while its longitudinal relaxation rate is sensitive to the local orientational mobility.

The water density and order, and the interaction between polymer and solvent molecules affect both quantities. The results were analyzed in terms of different physical models of self-diffusion and longitudinal relaxation of solvent. The mobility of water was further investigated in the presence of mono- and divalent counterions ( $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) in a physiological range of concentrations.

This article is organized as follows. After describing our experimental methodology, we briefly review various physical models of solvent self-diffusion and evaluate their applicability to describe the experimental data. In the next section, we focus on the analysis of the spin-lattice relaxation of water in salt free polyelectrolyte solutions and gels. This is followed by the discussion of the effect of added salts on the self-diffusion coefficient and spin-lattice relaxation rate of water.

## EXPERIMENTAL

### Materials

**Solution Preparation.** Aqueous solution of sodium polyacrylate (NaPA,  $M_w = 15$  kDa, concentration: 35% w/w) was purchased from Sigma–Aldrich. No further purification steps were performed. The NaPA solution was diluted by deionized water to the designated concentrations. Salts ( $\text{NaCl}$  or  $\text{CaCl}_2$ ) were added to the solutions during dilution.

### Gel Preparation

NaPA gels were made in aqueous solution by free-radical copolymerization of acrylic acid monomer and  $N,N'$ -methylenebis(acrylamide) cross-linker according to a procedure described previously.<sup>6</sup> The initial monomer concentration was 37% (w/w), and 31% of the monomers were neutralized by sodium hydroxide before polymerization. Dissolved oxygen was removed by bubbling nitrogen through the solution. Then, the monomer solution was diluted to the designated concentration and appropriate amounts of salts ( $\text{NaCl}$  or  $\text{CaCl}_2$ ) were added. Finally, potassium persulfate (0.5 g/L) was added to initiate the polymerization reaction, and the solution was placed in an oven at 70°C.

### Methods

**NMR-MOUSE.** The NMR measurements were made by a single-sided NMR system (Profile NMR-MOUSE, ACT GmbH, Germany). Single-sided NMR systems developed in the last two decades possess the advantages that they are portable and reliable to study relaxation times and diffusion coefficients of various samples.<sup>20</sup> They are widely used in diverse fields such as in the rubber and polymer industries, food and materials processing applications.<sup>20–25</sup>

A surface RF coil is placed on top of the magnet to excite and detect the NMR signal. The magnetic field strength at the selective volume is 0.32 T (corresponding to  $^1\text{H}$  Larmor frequency of 13.79 MHz), with a strong and highly uniform magnetic field gradient of 15.3 T/m across the selective volume. The Kea spectrometer and Prospa acquisition software are provided by Magritek, New Zealand. All NMR measurements were made at ambient temperature ( $23 \pm 1^\circ\text{C}$ ).

**Self-Diffusion Measurement.** Self-diffusion coefficients were measured by Hahn spin echoes ( $90^\circ\text{-}\tau\text{-}180^\circ\text{-}\tau\text{-echo}$ ) in the pres-

ence of a static and uniform magnetic field gradient.<sup>26</sup> To improve the sensitivity of these experiments, a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence was applied after the main diffusion-encoding period. The normalized signal attenuation for the Hahn echoes is,<sup>27</sup>

$$I/I_0 = \exp(-bD) \quad (1)$$

with

$$b = \frac{2}{3}(\gamma G)^2 \tau^3 \quad (2)$$

where  $\gamma$  is the gyromagnetic ratio of protons,  $G$  is the strength of the static magnetic field gradient,  $D$  is the self-diffusion coefficient, and  $\tau$  is the encoding period or echo time. Eight  $b$ -values ( $<1200$  s/mm<sup>2</sup>) were used to produce a diffusion decay curve with 1024 echoes being added and eight scans being performed for each  $b$ -value. This method was validated by measuring the self-diffusion coefficient ( $D$ ) of various solvents, such as water, methanol, ethanol.<sup>26</sup> All the diffusion decay curves were well fit by a single exponential function.

**Longitudinal Relaxation Time Measurement.** Longitudinal relaxation times ( $T_1$ ) were measured by using a saturation recovery sequence (saturation – recovery time  $\Delta$  – detection), followed by a CPMG train to improve the sensitivity, similar to the methods described above. Eight recovery times ( $\Delta$ ) were used to obtain a recovery curve, and eight scans for each recovery time, with 1024 echoes were added for each scan. The data were fitted to a mono-exponential function with a minor baseline.<sup>20</sup> The accuracy of our method was tested using a series of manganese chloride ( $\text{MnCl}_2$ ) solutions and we found reasonable agreement to literature values.<sup>28,29</sup>

## RESULTS AND DISCUSSION

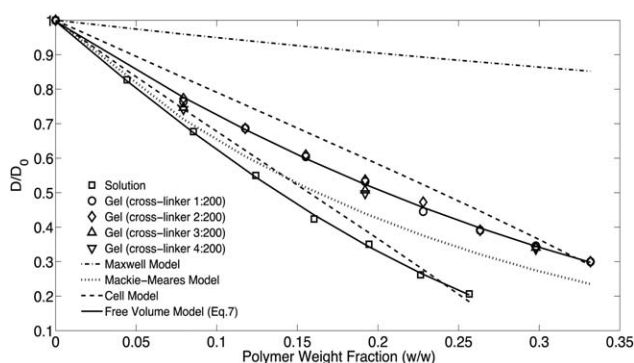
### Self-Diffusion Measurements in NaPA Solution and Gel as a Function of Polymer Concentration

Various physical models have been proposed to describe self-diffusion of solvent molecules in polymer gels and solutions. These models fall into three general categories: (1) obstruction, (2) hydrodynamic, and (3) free volume<sup>30</sup>.

First we analyze the experimental data using two obstruction models: the Maxwell,<sup>30</sup> and the Mackie–Meares model.<sup>31</sup> Then, the validity of the cell model, a combination of obstruction and hydration models, is tested<sup>32</sup>. Finally, we apply the Vrentas–Duda free-volume model.<sup>33</sup>

Figure 1 shows the results obtained for NaPA solutions and gels in the absence of added salt. It can be seen that  $D$  is significantly greater in the gel than in the corresponding solution, and is practically independent of the crosslink density.

**Obstruction Models.** In the obstruction models, the polymer chains are considered to be impenetrable and motionless relative to the small diffusing solvent molecules. The polymer hinders the diffusion of water molecules, increasing the path length required by a geometric tortuosity factor. Consequently, the apparent self-diffusion coefficient of small molecules decreases. In these models, no interaction between the polymer and solvent molecules is taken into account. The obstruction effect is closely related to the shape of the obstructers; rod-like shapes



**Figure 1.** Self-diffusion coefficient  $D$  of NaPA solutions and gels with various cross-link densities normalized by the self-diffusion coefficient of the pure water  $D_0$ . The curves are fits of solution data and gel data with crosslink density 1 : 200 by different models (see text).

obstruct more than spheres.<sup>34</sup> There are two main diffusion models based exclusively on the obstruction effect, (1) the Maxwell model, which assumes that the obstructers are spheres, and (2) the Mackie–Meares model,<sup>31</sup> where the polymer chains are assumed to be impenetrable, motionless, infinitely long rods.

In the Maxwell model the self-diffusion coefficient  $D$  of the solvent is expressed as,<sup>28</sup>

$$\frac{D}{D_0} = \frac{1}{1 + \Phi/2} \quad (3)$$

where  $D_0$  is the self-diffusion coefficient of the pure solvent and  $\Phi$  is the volume fraction of the polymer

$$\Phi = \frac{m^{\text{poly}} \nu^{\text{poly}}}{m^{\text{poly}} \nu^{\text{poly}} + m^{\text{water}} \nu^{\text{water}}} \quad (4)$$

In eq. (4),  $m^{\text{poly}}$  is the mass and  $\nu^{\text{poly}}$  ( $= 0.82 \text{ cm}^3/\text{g}$ ) is the specific volume of NaPA, and  $m^{\text{water}}$  and  $\nu^{\text{water}}$  are the mass of water and its specific volume, respectively.

The Mackie–Meares model yields the expression:<sup>31</sup>

$$\frac{D}{D_0} = \left[ \frac{1 - \Phi}{1 + \Phi} \right]^2 \quad (5)$$

Figure 1 clearly shows that the obstruction models do not adequately describe the concentration dependence of the self-diffusion coefficient. The Maxwell model seriously underestimates the obstruction effect of the NaPA. In contrast, the Mackie–Meares model reproduces the self-diffusion of water at low polymer concentration ( $c < 10\%$  w/w) relatively well. The failure of these two obstruction models at high polymer concentrations may be due to either the complex geometry of the polymer chain or hydration effect that slows down water self-

diffusion.<sup>30,35</sup> The gel data fall between the Maxwell and Mackie–Meares models. The reduced obstruction effect for the gel suggests that crosslinking may alter the effective geometry of the polymer chains with respect to water diffusion.

**Combined Obstruction and Hydration Model.** A possible reason for the failure of obstruction models is that the interaction between water and polymer slows down the water self-diffusion close to the polymer. The cell-diffusion model of Jönsson et al. takes into account both obstruction and hydration effects.<sup>32</sup> The model successfully predicts the self-diffusion of water in casein dispersions,<sup>36</sup> in various surfactant–water systems,<sup>37</sup> and also in whey protein solutions.<sup>38</sup> The macroscopic system is divided into identical cells containing one polymer molecule surrounded by water. In each cell, a distinction is made between hydration water and bulk water that may have different densities and mobilities. The macroscopic self-diffusion constant is represented by an apparent diffusion coefficient obtained by solving the diffusion equations for the cell with appropriate boundary conditions.<sup>32,38</sup> The cell model yields for a solution of spherical particles

$$D_{\text{eff}} = D_0 \left( 1 + 0.75 \frac{m^{\text{poly}}}{m^{\text{water}}} \right) \frac{\left( 1 + 0.75 \frac{m^{\text{poly}}}{m^{\text{water}}} - k \frac{m^{\text{poly}}}{m^{\text{water}}} \right)}{1 + 0.75 \frac{m^{\text{poly}}}{m^{\text{water}}} + 0.5 \frac{m^{\text{poly}}}{m^{\text{water}}}} \quad (6)$$

where  $k$  is a fitting parameter.

Equation 6 was used to fit the NaPA solution and gel (with cross-link density 1 : 200) data with different values of  $k$ . Figure 1 shows that this model fails to estimate the experimental diffusion coefficients over the entire concentration range. The observed discrepancy may be related to the deviation of the geometry of the NaPA chains from the assumed spherical shape.

**Free Volume Model.** The free volume model is based on the concept that molecular transport is mainly governed by the occurrence of two events: (1) a hole of sufficient size (free volume) should appear adjacent to the small molecule, and (2) the molecule should have enough energy to jump into it.<sup>39</sup> The polymer reduces the free volume of the solution, which explains the observed decrease in the solvent self-diffusion coefficient with increasing polymer concentration.<sup>40</sup> This model satisfactorily describes self-diffusion of small molecules in numerous polymer solutions such as (polyvinyl acetate)–toluene,<sup>41</sup> polystyrene–benzene systems,<sup>42,43</sup> water–gelatin,<sup>44</sup> water–PEG,<sup>45</sup> and water–Poly(*N,N*-dimethylacrylamide) (PDMAA) gels.<sup>46</sup>

The Vrentas–Duda theory<sup>33,47</sup> predicts that the self-diffusion coefficient of small molecule (solvent) in a binary system is

$$\frac{D}{D_0} = \exp \left\{ \frac{-(w_1 \hat{V}_1^* + w_2 \xi \hat{V}_2^*)}{\left( \frac{K_{11}}{\gamma} \right) w_1 (K_{21} - T_{g1} + T) + \left( \frac{K_{12}}{\gamma} \right) w_2 (K_{22} - T_{g2} + T)} - \frac{-\hat{V}_1^*}{\left( \frac{K_{11}}{\gamma} \right) (K_{21} - T_{g1} + T)} \right\} \quad (7)$$

where  $w_1$  and  $w_2$  are the weight fractions of the solvent and the polymer,  $T$  is the absolute temperature, and  $K_{11}$ ,  $K_{12}$ ,  $K_{21}$ ,  $K_{22}$ ,  $T_{g1}$ ,  $T_{g2}$ ,  $\hat{V}_1^*$ ,  $\hat{V}_2^*$ ,  $\xi$ ,  $\gamma$  are constants (free volume parameters of

polymer and solvent). For water the free volume parameters known from the literature<sup>44</sup> are listed in Table I. The two independent parameters for the polymer,  $\xi \hat{V}_2^*$  and

**Table I.** Parameters Used and Obtained in Free Volume Model

Parameters	Values	Notes
$K_{11}/\gamma$ ( $\text{cm}^3 \text{g}^{-1} \text{K}^{-1}$ )	$2.33 \times 10^{-3}$	From Ref. 44
$K_{21} - T_{g1}$ (K)	-156.9	From Ref. 44
$\dot{V}_1^*$ ( $\text{cm}^3 \text{g}^{-1}$ )	1.071	From Ref. 44
$\xi \dot{V}_2^*$ ( $\text{cm}^3 \text{g}^{-1}$ )	$0.95 (\pm 0.10)$	By fitting eq. (7) (in solution)
$\xi \dot{V}_2^*$ ( $\text{cm}^3 \text{g}^{-1}$ )	$1.37 (\pm 0.10)$	By fitting eq. (7) (in gel)
$K_{12}(K_{22} - T_{g2} + T)/\gamma$ ( $\text{cm}^3 \text{g}^{-1}$ )	$-0.01 (\pm 0.02)$	By fitting eq. (7) (in solution)
$K_{12}(K_{22} - T_{g2} + T)/\gamma$ ( $\text{cm}^3 \text{g}^{-1}$ )	$0.16 (\pm 0.02)$	By fitting eq. (7) (in gel)

$(K_{22} - T_{g2} + T)K_{12}/\gamma$ , were obtained by fitting eq. (7) to the experimental data.

Figure 1 also shows the fits of eq. (7) (solid line) to the NaPA solution and gel (with cross-link density 1 : 200) data. In Table I, the fitting parameters of eq. (7) are listed. In both systems, the agreement between the prediction of eq. (7) and the experimental data is reasonable. The difference in the fitting parameters may reflect the presence of cross-links. Cross-linking causes the redistribution of the polymer chains and modifies the thermodynamics of the polymer/solvent system.<sup>48,49</sup> However, further experiments and theories are needed to understand the underlying physical difference between the polymer solution and gel and the influence on water self-diffusion.

It might be that obstruction effects dominate water self-diffusion in NaPA solutions and gels at low polymer concentrations, while at high polymer concentrations, the interaction between polymer and solvent molecules becomes non-negligible.  $D$  is observed to be greater in gels than in polymer solutions at the same concentration, and although the free-volume models satisfactorily describe the water self-diffusion data, the underlying physical mechanisms for the difference remain unclear.

In what follows we investigate the effect polymer concentration and ions on the spin-lattice relaxation of water in NaPA solutions and gels.

### Spin-Lattice Relaxation Time, $T_1$ , in Sodium Polyacrylate Solution and Gel as a Function of Polymer Concentration

In water-polymer systems two types of water are present: (1) polymer-associated water; and (2) "free" water that is not influenced by the presence of the polymer. The spin-lattice relaxation rate of water is sensitive to both the structure of the polymer and the interaction between the polymer and water. Neutron and X-ray scattering measurements indicate that the density of water is greater near the polymer than in the bulk.<sup>50</sup> It was also reported that the translational and orientational mobility of polymer-associated water was slower than that of the free water, and orientation became anisotropic due to interaction with macromolecules.<sup>51</sup>

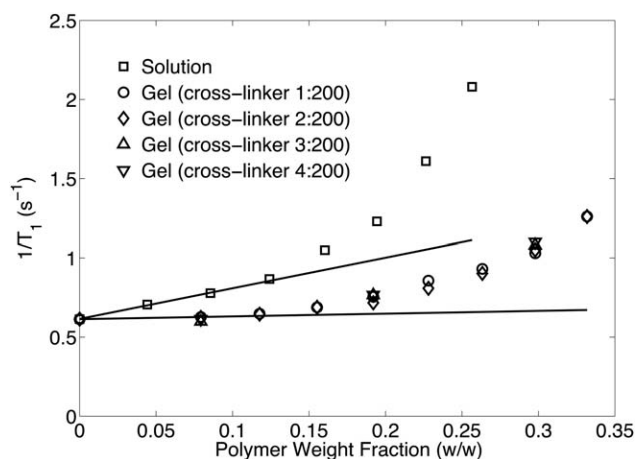
In polymer systems, the relaxation behavior of water nuclei has been described in terms of a fast-exchange two-site model.<sup>52-54</sup> The effective spin-lattice relaxation rate is given by<sup>55,56</sup>

$$\frac{1}{T_{1,eff}} = \frac{f_b}{T_{1,b}} + \frac{1-f_b}{T_{1,f}} \quad (8)$$

where  $f_b$  and  $T_{1,b}$  are the fraction and average longitudinal relaxation time of polymer-associated water, and  $1 - f_b$  and  $T_{1,f}$  are the fraction and longitudinal relaxation time of the free water.

In Figure 2, we plot the spin-lattice relaxation rate  $1/T_1$  as a function of the polymer concentration. The data indicate that at low polymer concentration, the dependence of spin-lattice relaxation rate on polymer concentration can be approximated as linear. This finding implies that  $T_{1,b}$  is constant and  $f_b$  is proportional to the fraction of the polymer. At higher concentrations (above 0.12 g/g in the solution and gel), however,  $1/T_1$  increases faster than linear. Similar behavior was reported for other polyelectrolyte solutions such as low molecular weight PAA-water,<sup>51</sup> protein-water,<sup>38</sup> and  $\beta$ -lactoglobulin-water solutions.<sup>57</sup> Based on the two-site model, the deviation from linearity may be caused either by the increased number of polymer-associated water molecules or the faster relaxation rate  $1/T_{1,b}$  of this water.

In summary, the results show that  $D$  is greater and the relaxation time  $T_1$  is longer in the gel than in the polymer solution at the same concentration. These findings imply that the cross-linked polymer has a smaller effect on water mobility than its



**Figure 2.** Variation of the spin-lattice relaxation rate  $1/T_1$  as a function of the NaPA weight fraction in solutions and gels with various cross-link densities. Continuous lines are fits of eq. (10) to the experimental data.

**Table II.** Self-Diffusion and Spin–Lattice Measurements on NaPA Solutions and Gels in Pure Water and in NaCl Solutions

Polymer concentration (w/w)	NaCl concentration (M)	$D$ ( $10^{-9}$ m <sup>2</sup> /s)	$1/T_1$ (s <sup>-1</sup> )
0% (solution)	0	2.12 (0.02)	0.56 (0.02)
0% (solution)	1.0	2.06 (0.02)	0.55 (0.02)
16% (solution)	0	1.16(0.01)	0.89(0.02)
16% (solution)	0.6	1.11(0.01)	0.92(0.02)
26% (gel)	0	0.99(0.01)	0.85(0.02)
26% (gel)	0.6	0.91(0.01)	0.89(0.02)

uncrosslinked counterpart. The variation of the cross-link density of the gel does not have significant effect on either  $D$  or  $1/T_1$ .

There are two possible explanations for the difference of solvent mobility between the uncrosslinked polymer and the crosslinked state: (1) the solvent mobility is dependent on polymer molecular weight, which changes from limited value in solution (15 kDa) to infinite in the gel. However, in concentrated polymer solutions (above 0.12 g/g), the effect of polymer molecular weight should be minimal due to the strongly overlapped chains. Previous experiments on small molecule self-diffusion in polymer solutions as a function of polymer molecular weight showed solvent mobility is independent of, or only weakly dependent on polymer molecular weight especially when the chains are high molecular weight.<sup>45,58</sup> In the present study, NaPA with 15 kDa was chosen to avoid this effect. (2) The cross-linking process modifies the chemical properties of polymer chains and the polymer–solvent interaction. Our present observation is consistent with evidence from previous macroscopic differences between the two states, and these changes are not simply proportional to the number of cross-linking points.<sup>48,59,60</sup> Osmotic pressure measurements on poly(vinyl acetate) gel were found to be almost independent of the cross-linking density of the gel.<sup>48</sup> A similar change of the self-diffusion coefficient from the uncrosslinked state to the crosslinked state was also reported for polydimethylsiloxane (PDMS)–toluene systems.<sup>59</sup> The difference was attributed to

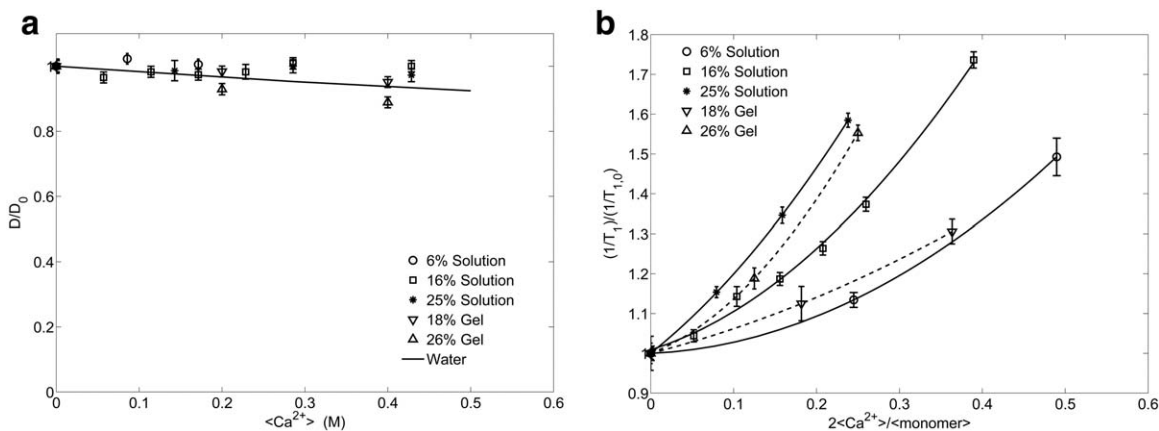
structural inhomogeneities created by the crosslinking process. During crosslinking polymer rich regions are formed, which coexist with regions of diminished polymer concentration. The NaPA gels have been observed to contain large inhomogeneities (greater than 1000 Å) as detected by small-angle neutron scattering measurements.<sup>61</sup> More experiments are needed to validate these hypotheses and elucidate the underlying chemical and physical mechanisms.

#### Effect of Ions on the Dynamic Properties of Water in NaPA Solutions and Gels

We determined the self-diffusion coefficient and the longitudinal relaxation rate of water in polymer-free salt solutions<sup>62</sup> and in NaPA solutions and gels. The data listed in Table II show that monovalent salt (NaCl) has no significant effect on  $D$  and  $1/T_1$ .

Addition of divalent salt ( $\text{CaCl}_2$ ) slightly modifies the self-diffusion coefficient [Figure 3(a)] and significantly enhances the longitudinal relaxation rate [Figure 3(b)]. The latter increases by more than 70% as the  $\text{CaCl}_2$  concentration varies from 0M to 0.4M. The curves in Figure 3(b) can be satisfactorily described by a second-order polynomial. The results also indicate that the enhancement of  $1/T_1$  is more pronounced at higher polymer concentration (at constant  $\text{CaCl}_2$  concentration).

The data shown in Figure 3(a,b) reveal important differences between the effects of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions on the mobility of water. The weak influence of NaCl suggests that the diffuse



**Figure 3.** (a) Self-diffusion coefficient and (b) spin–lattice relaxation rate as a function of  $\text{CaCl}_2$  concentration in both NaPA solutions and gels (cross-link density 2 : 200). All the data are normalized by the initial values.

monovalent ion cloud does not affect the conformation of the polymer and the interaction between the polymer and solvent. In the case of  $\text{Ca}^{2+}$  ions, the increased spin–lattice relaxation rate reflects the more effective charge compensation when calcium ions replace sodium ions.

Previous studies indicate that ions in polyelectrolyte systems affect the thickness and degree of order of the polymer-associated hydration shell.<sup>63–66</sup> Increasing salt concentration may decrease the hydration strength due to increased screening of charges on the polymer backbone.<sup>63</sup> Reduction of the hydration stress increases both the self-diffusion coefficient and relaxation time. However, the observed reduction of the relaxation time shows that in the present system the interaction between  $\text{Ca}^{2+}$  and NaPA has no significant effect on the hydration strength between charged polymer and water.

Recent molecular dynamics simulation and anomalous small-angle X-ray scattering measurements show that divalent cations are preferentially condensed onto oppositely charged polyelectrolyte chains while monovalent cations move more freely.<sup>9,67</sup> In calcium ion containing systems the orientational mobility of the polyelectrolyte molecule may be slowed due to electrostatic attraction between the calcium ion and two negative charges on the polymer backbone, which may further slow the tumbling rate of polymer-associated water molecules and result in a shorter relaxation time.

## CONCLUSIONS

The self-diffusion coefficient and longitudinal relaxation rate of water in NaPA solutions and gels were determined by NMR. The self-diffusion measurements were analyzed in terms of different physical models of solvent self-diffusion in polymer systems. It was found that the free volume model provides a satisfactory fit of both solution and gel results.

To describe the relaxation response of water a linear two-site fast exchange model was adopted. In gels the self-diffusion coefficient is greater and the relaxation time of water is longer than in the corresponding (uncrosslinked) polymer solutions. The observed difference can be attributed to chemical and structural changes caused by cross-linking, however their influence on solvent mobility is almost independent of the number of cross-linking points.  $\text{Na}^+$  only slightly affects the relaxation rate and self-diffusion coefficient of water. Addition of  $\text{Ca}^{2+}$  enhances the relaxation rate but only weakly modifies the self-diffusion coefficient. Further studies are required to understand the differences between the dynamic behavior of polyelectrolyte gels and solutions and to clarify the effect of monovalent and divalent cations on the NMR relaxation properties of charged polymer systems.

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