Swelling/deswelling of polyacrylamide gels in aqueous NaCl solution: Light scattering and macroscopic swelling study

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Abstract. Swelling kinetics of water-swollen polyacrylamide (PAAm) hydrogels (WSG) was investigated in various concentrations of aqueous NaCl by macroscopic swelling measurements. For lower concentration of NaCl, WSG showed exponential swelling whereas at higher concentration of NaCl it underwent deswelling at short times and exponential swelling at long times. From these studies, collective diffusion coefficient, D, of the polymer network and polymer–solvent interaction parameter, χ, were calculated and found to decrease with increase in [NaCl]. Collective diffusion coefficients measured from dynamic light scattering (DLS) and that obtained from macroscopic swelling measurements are found to agree well. Measured ensemble-averaged dynamic structure factor $f(q, t)$ for WSG and salt-swollen gels (SSG) showed an initial decay followed by a plateau at long times and it can be described by harmonically bound Brownian particle (HBBP) model. Enhanced scattering intensity at low scattering angles using static light scattering (SLS) measurements revealed the presence of inhomogeneities in PAAm gels. The reasons for increased scattering intensity of SSG over WSG gel and the linear decrease of D with increase in NaCl concentration are explained.

1. Introduction

Polymer hydrogels consist of hydrophilic network of polymer strands that are cross-linked by chemical or physical bonding and are insoluble in any solvent [1–3]. Their swelling and deswelling ability can be tuned by the interaction between the polymeric network and the solvent. Properties of the gel are studied by varying the stimuli such as solvent composition [1], temperature [4], electric field [5], ionic strength [6], and pH [7] that

perturb their swelling and deswelling behaviour. Hydrogels have been used as temperature and pH sensors [8], biosensors [9], memory devices [10], chemical sensors [11] and optical switches [12] by immobilizing Bragg diffracting mesoscopically periodic array of colloidal particles and functionalizing the hydrogel backbone with specific molecular recognition agents. Further, crown ether-functionalized polyacrylamide (PAAm) hydrogels have been used to separate specific ions from high level liquid nuclear waste which is in nitric acid [13]. Thus, study on swelling and deswelling behaviour of PAAm hydrogels in different solvents is important and here we report the swelling and deswelling behaviour of PAAm hydrogel in different concentrations of aqueous NaCl solution.

The effect of aqueous NaCl solutions on the equilibrium swelling behaviour of PAAm-based ionic hydrogels was studied in the past using macroscopic equilibrium swelling experiments [6,14,15]. For example, equilibrium swelling behaviour of PAAm-based polyelectrolyte gel [6] in aqueous NaCl solutions (10^{-5}–1 M) and PAAm-based ampholytic gels [14] in aqueous NaCl solutions (10^{-5}–5 M) have been studied. Degree of swelling (DoS) of polyelectrolyte gels was found to decrease with increase in concentration of aqueous NaCl solution. But the ampholytic gels showed anti-polyelectrolyte behaviour; DoS was found to increase with increase in NaCl concentration from 0.1 to 5 M. Swelling of PAAm gel is independent of NaCl concentration from 10^{-5} to 0.1 M and it was found to increase with further increase in NaCl concentration from 0.1 to 5 M [6,14,15]. Swelling behaviour of polyelectrolyte and ampholytic gels in NaCl were explained respectively by Flory theory with ideal Donnan equilibrium and Debye–Huckel theories. But the interpretation is not satisfactory for the swelling of PAAm gel in higher concentration (>0.1 M) of NaCl. Further, there are no studies on swelling kinetics of PAAm gels in aqueous NaCl solution and reversible swelling behaviour of salt-swollen gel (SSG) in water. Here we report detailed static and dynamic light scattering studies as well as macroscopic swelling kinetics measurements on disc-shaped PAAm hydrogels in a wide range of NaCl concentrations. Deswelling kinetics of SSG in water is also presented. For the first time, macroscopic swelling results are compared with the results obtained from dynamic light scattering (DLS) technique. Polymer–solvent parameter χ and collective diffusion coefficient D are found to decrease with increase in NaCl concentration and reasons for this salt dependence are explained. The important finding of our study is that high salt concentrations have strong influence on PAAm hydrogel swelling and our results indicate that the decrease in polymer–polymer affinity with increase in salt concentration is responsible for the swelling.

2. Experimental methods

2.1 *Synthesis*

PAAm hydrogels were prepared [16] by photopolymerization using a monomer solution containing 10% w/w acrylamide (AAm) (99%, Merck) and 0.5 or 1% w/w N,N′-methylene bisacrylamide (MBA) (99%, Ottokemi). 1 μl of photoinitiator 2,2′-diethoxyacetophenone (DEAP) (98%, Acros Organics) was added for every 1 ml of the deionized monomer solution. To prepare hydrogel in disc shape, the mixture was injected into a quartz cell consisting of two quartz plates separated by a circular neoprene gasket

of 3 mm thickness and 43 mm internal diameter and exposed to 360 nm soft UV rays from 300 W UV/Vis lamp (Osram) for 2 h. After polymerization, hydrogel was kept in water for a week to reach equilibrium. For light scattering measurements, samples were prepared in 8 mm diameter quartz cylindrical cells. For light scattering studies, the pre-gel solution was filtered using 0.1 μm Millipore syringe filter. PAAm hydrogels with 0.5% MBA are transparent while PAAm gels with 1% MBA are opaque. So the former was used for light scattering measurements.

2.2 *Swelling and deswelling measurements*

Swelling kinetics of water-swollen gel (WSG) was studied by transferring the WSG gels to petridishes containing 50 ml NaCl solutions having 1, 2, 3, 4 and 5 M concentration. The deswelling kinetics of SSG in water was studied by immersing SSG in 50 ml deionized water. During both swelling and deswelling, weight of the gel was measured as a function of time for determining the degree of swelling (deswelling) DoS (DoD). DoS is defined as

$$\text{DoS} = \frac{W_{t,\text{NaCl}} - W_0}{W_0}, \tag{1}$$

where $W_{t,\text{NaCl}}$ is the weight of WSG at time t in NaCl solution and W_0 is the equilibrated weight of the hydrogel in water at $t = 0$. Similarly, DoD is defined as

$$\text{DoD} = \frac{W_{t,\text{H}_2\text{O}} - W_0}{W_0}, \tag{2}$$

where $W_{t,\text{H}_2\text{O}}$ is the weight of SSG at time t in deionized water.

Diameter (d) and thickness (h) of the gels were measured after reaching swelling equilibrium to estimate the collective diffusion coefficient D of the gels. Though the swelling equilibrium is reached in about 33 h from the time of transferring the WSG to NaCl solutions ($t = 0$), all the gels were kept in NaCl solutions for seven days and then transferred to water for carrying out deswelling studies.

2.3 *Static and dynamic light scattering measurements*

Static light scattering (SLS) and dynamic light scattering (DLS) measurements were carried out on WSG and SSG using a Malvern 4700 (Malvern Instruments, UK) light-scattering set-up equipped with a goniometer, a multi-tau correlator, a photomultiplier tube (PMT) and a 250 mW diode-pumped vertically polarized solid-state laser operating at a wavelength $\lambda = 532$ nm. The scattered intensity was collected using a vertically aligned Glan–Thomson prism placed in front of the PMT. The time-averaged intensity–intensity autocorrelation function (ICF) $g_\text{T}^{(2)}(q, t)$ was measured at different scattering wave vectors $q = (4\pi n/\lambda) \sin(\theta/2)$, where n is the refractive index of the gel, θ is the scattering angle and λ is the wavelength of incident laser beam using a multi-tau correlator. Ensemble-averaged scattered intensities $\langle I(q) \rangle_\text{E}$ at different scattering angles were measured by rotating the sample at a speed of 2 rpm using a computer-controlled stepper motor. SLS measurements were carried out by measuring $\langle I(q) \rangle_\text{E}$ as a function of scattering angle. Time-averaged intensity $\langle I(q) \rangle_\text{T}$ and ensemble averaged intensity $\langle I(q) \rangle_\text{E}$ were measured for 10 min.

As hydrogel exhibits non-ergodicity, we have determined ensemble-averaged dynamic structure factor $f(q, t)$ from $g_T^{(2)}(q, t)$, $\langle I(q) \rangle_T$ and $\langle I(q) \rangle_E$ using Pusey and van Megen method [17,18]. The time-averaged ICF, $g_T^{(2)}(q, t)$, is related to the $f(q, t)$ by

$$f(q, t) = \frac{Y - 1}{Y} + \frac{(g_T^{(2)}(q, t) - \sigma_I^2)^{1/2}}{Y},\tag{3}$$

where σ_I^2 is the mean-square intensity fluctuation given by $\sigma_I^2 = \langle I^2(q) \rangle_T / \langle I(q) \rangle_T^2 - 1$ and the parameter $Y = \langle I(q) \rangle_E / \langle I(q) \rangle_T$.

2.4 *Flory–Huggin's theory of swelling*

According to Flory–Huggin's theory, when the as-prepared non-ionic hydrogel is immersed in a solvent and allowed to reach equilibrium with its surroundings, two forces act on the hydrogel [19,20]. One is the osmotic pressure arising from mixing of hydrogel network with the solvent and the other is the osmotic pressure from network elasticity. Osmotic pressure due to mixing, Π_M, is given as

$$\frac{\Pi_M}{RT} = -\frac{1}{V_{H_2O}} \left[\ln \left[1 - \left(\frac{V_0}{V} \right) \right] + \left(\frac{V_0}{V} \right) + \chi \left(\frac{V_0}{V} \right)^2 \right].\tag{4}$$

Osmotic pressure arising from network elasticity, Π_E, can be written as

$$\frac{\Pi_E}{RT} = -\frac{v_e}{V_m} \left[\left(\frac{V_m}{V} \right)^{1/3} - \frac{1}{2} \left(\frac{V_m}{V} \right) \right],\tag{5}$$

where R is the universal gas constant, T is the temperature, V_{H_2O} is the molar volume of the water, V_0 is the volume of the dry gel, V is the volume of the swollen hydrogel, χ is the Flory–Huggins polymer–solvent interaction parameter, v_e is the effective number of cross-linked chains in the network and V_m is the volume of the as-prepared hydrogel. At swelling equilibrium, these two osmotic pressures will be equal but opposite to each other. Hence, the total osmotic pressure will be zero.

$$\Pi_T = \Pi_M + \Pi_E = 0.\tag{6}$$

Bulk modulus of the polymer network is given as [19,20]

$$K = \frac{3 v_e}{V_m} RT.\tag{7}$$

The effective number of cross-linked chains, v_e, in the WSG has been estimated from eqs (4)–(6) using the measured values of V_m, V, V_0 and taking χ [10] to be 0.503. The estimated effective numbers of cross-linked chains, v_e, for 0.5 and 1% gels are 5.46×10^{-5} and 8.97×10^{-5} moles respectively. This corresponds to an effective cross-linked chain fraction of 0.36 and 0.30 for 0.5 and 1% gels respectively. The effective cross-linked chain fraction, v', is defined as the ratio of the amount of cross-linker used in effective cross-link to the total amount of cross-linker taken for gelation. Using the value of v_e, the bulk modulus of the hydrogel network was estimated from eq. (7). Bulk moduli of 0.5 and 1% MBA gels are found to be 9.3×10^4 and 1.5×10^5 N/m^2 respectively.

3. Results and discussion

3.1 *Macroscopic swelling/deswelling studies*

3.1.1 *Swelling kinetics.* Figure 1 shows the time dependence of DoS for 0.5 and 1% MBA WSG at various concentrations of NaCl. WSG exhibited exponential swelling at lower concentrations of NaCl (<3 M), but underwent deswelling at short times (see insets) and swelling at longer times at higher concentrations (≥3 M) of NaCl. The swelling time constant τ_s is estimated by fitting the swelling data to the expression

$$\text{DoS} = \text{DoS}_{\text{max}} - A_s \exp\left(\frac{-t}{\tau_s}\right) \tag{8}$$

given by Li–Tanaka theory [19] for a disc-shaped gel. Here, DoS_{max} is the maximum degree of swelling, A_s is the amplitude of swelling and t is the time. When WSG is
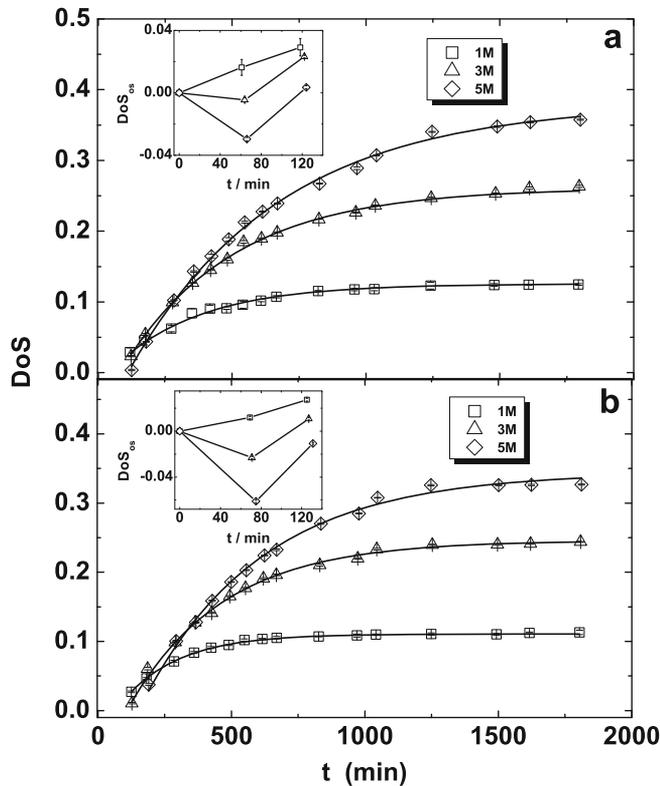

Figure 1. Degree of swelling of (**a**) WSG with 0.5% MBA and (**b**) WSG with 1% MBA in different concentrations of NaCl solution. Solid curves are the fits to eq. (8). For clarity, only data corresponding to three concentrations were plotted. Insets represent short-time deswelling behaviour of the gels due to osmosis.

immersed in NaCl solution, the ionic solution pulls the water from the gel due to the osmosis effect. Hence, the gel exhibits deswelling at short times (inset of figure 1). As the time proceeds, the Na^+ and Cl^- ions diffuse into the gel due to the concentration gradient, the osmosis effect ceases and mixing dominates resulting in the exponential swelling of the gel. Further, it can also be seen that DoS depends strongly on the concentration of NaCl. Present observations are consistent with those reported earlier [6,14,15]. To understand the PAAm gels swelling at higher concentrations of NaCl, we have estimated polymer–solvent interaction parameter χ at swelling equilibrium for each gel in NaCl solution using eqs (4)–(6) and its variation with NaCl concentration is shown in figure 2. It can be seen from figure 2 that the polymer–solvent interaction parameter decreases with increase in [NaCl] and it also depends on the concentration of the cross-linker. The decrease of χ with increase in [NaCl] implies decrease in polymer–polymer affinity or, in other words, increase in hydrophilicity. Polymer–polymer affinity decreases due to electrostatic screening by Na^+ and Cl^- ions forming an electric double layer around the polar groups such as C=O and C–N. This decrease in polymer–polymer affinity causes the gel to swell in NaCl solutions. As the concentration of the ions in the solution increases, DoS of both 0.5 and 1% gels increases due to increased screening resulting in PAAm network to turn more hydrophilic and causing increased swelling with increase in NaCl concentration. It may be mentioned here that 0.5% MBA gel has lesser number of cross-linked chains (ν_e) compared to 1% MBA gel. So, the bulk modulus of 0.5% MBA gel is lower when compared to 1% MBA gel. Hence 0.5% MBA gel exhibits more swelling than 1% MBA gel at a given NaCl concentration. We indeed observe on an average about 12% more swelling (note from figure 1 that DoS values increase as time increases for 0.5% MBA gel compared to 1% MBA gel for all concentrations of NaCl) of 0.5% MBA gel than that for 1% MBA gel. For the same reason, 1% MBA gel deswell more initially (see insets of figure 1) compared to 0.5% MBA gel.
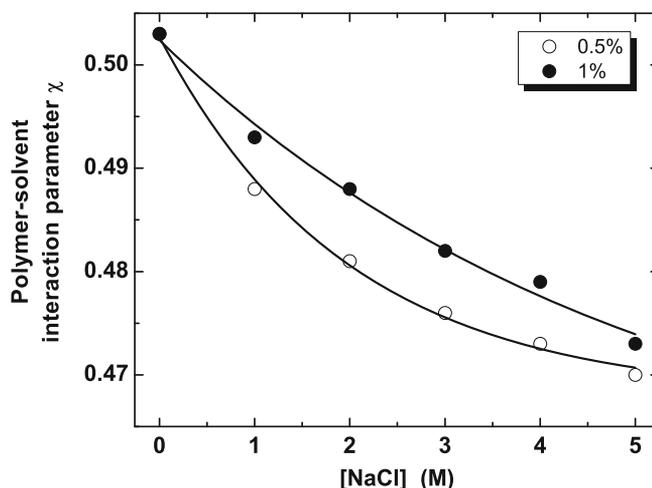

Figure 2. Polymer–solvent interaction parameter χ vs. [NaCl] for 0.5% and 1% MBA gels. The curves are guides to the eye.

3.1.2 *Deswelling kinetics.* After swelling equilibrium in NaCl solution is reached, gels were transferred to deionized water to study their deswelling kinetics. DoD of SSG in deionized water as function of time is shown in figure 3. Here, the reverse processes happen, i.e., Na$^+$ and Cl$^-$ ions present in the SSG diffuse out of the gel into the water due to the concentration gradient. The screening comes down resulting in an increase in the polymer–polymer affinity. Hence the gel deswells. The deswelling data as a function of time is found to fit (figure 3) to the following expression:

$$\text{DoD} = \text{DoD}_{\text{max}} + A_d \exp\left(\frac{-t}{\tau_d}\right),\tag{9}$$

where DoD_{max} is the maximum degree of deswelling, A_d is the amplitude of deswelling and τ_d is the deswelling time constant. It can be seen from figure 3 that SSG at low concentration of NaCl deswells to its original water-swollen state, but not SSGs at high concentration of NaCl. This might be due to the retention of ions by the gel.

Figure 4 shows swelling (τ_s) and deswelling (τ_d) time constants extracted respectively from the fits to eqs (8) and (9). Both time constants show a linear increase with increase
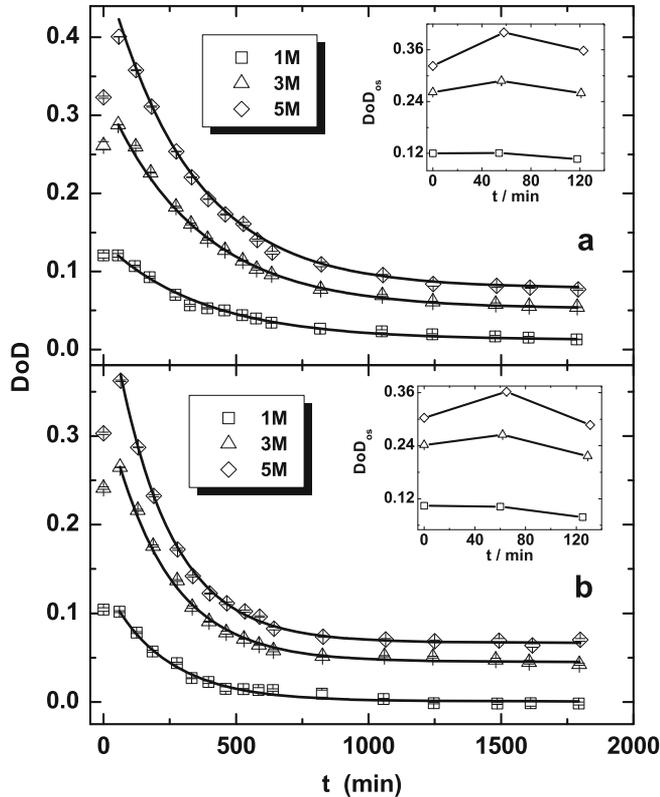

Figure 3. Degree of deswelling of (**a**) SSG with 0.5% MBA and (**b**) SSG with 1% MBA in water. Solid curves are the fits to eq. (9). For clarity, only data corresponding to three concentrations were plotted. Insets represent short-time swelling behaviour of the gels due to osmosis.
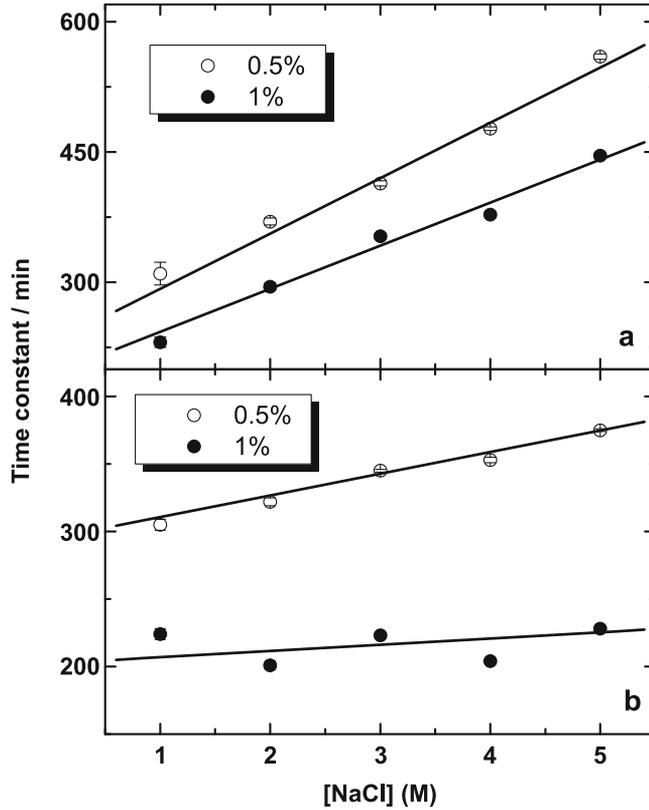
Figure 4. Time constant vs. [NaCl] for 0.5% and 1% MBA gels. (**a**) Swelling (τ_s) and (**b**) deswelling (τ_d). Lines are guides to the eye.

in NaCl concentration. We also observe that swelling and deswelling time constants of 0.5% gel are considerably higher than those for 1% gel. To understand this behaviour, we determine the collective diffusion coefficient D of the gel network [21] (which is also a measure of the diffusion of the NaCl solution into the gel against the friction offered by the polymer network) using the expression

$$D = \frac{h^2}{\left(\tau \pi^2 \left(1 + (\mu/M_{os})\right)\right)}, \tag{10}$$

where h is the gel thickness in NaCl solution at swelling equilibrium ($t \sim 33$ h), μ is the shear modulus which is given by [22]

$$\mu = \frac{(3 - 6\nu) K}{2 (1 + \nu)} \tag{11}$$

and osmotic pressure modulus is given as [21]

$$M_{os} = K + \frac{4}{3}\mu. \tag{12}$$

In eq. (11) ν (=0.457 for PAAm gels [23]) represents the Poisson's ratio and is known to be independent of cross-linker concentration [24]. D was estimated using eqs (10)–(12) for different concentrations of NaCl solution and is plotted as a function of [NaCl] in figure 5. It can be seen that D decreases linearly with [NaCl] for both gels and D is higher for 1% gel than that for 0.5% gel. The latter observation is consistent with the earlier reports [25]. It is known from small-angle neutron scattering studies that the correlation length is high for 1% gel than that for 0.5% gel [26]. Hence, ions can diffuse faster in 1% gel than in 0.5% gel.

3.1.3 *Light scattering studies.* As static and dynamic light scattering studies provide a microscopic picture on the structure and dynamics of the gel network, we have carried out these studies on 0.5% MBA WSG and SSG (5 M NaCl). Since gels are known to exhibit non-ergodicity, we employed Pusey and van Megen method [17,18] for obtaining the ensemble-averaged dynamic structure factor $f(q, t)$ from the time-averaged intensity autocorrelation function $g_{\mathrm{T}}^{(2)}(q, t)$ as mentioned in the experimental section. The dynamic structure factors thus obtained for different values of q are shown in figure 6. It can be seen that $f(q, t)$ exhibits an initial decay followed by a plateau. The correlation function at long times $f(q, \infty)$ (i.e. the plateau) depends on the scattering wave vector q, i.e., implying that the dynamics is describable by the harmonically bound Brownian particle (HBBP) model. According to this model [27,28], the dynamic structure factor $f(q, t)$ is given by the equation

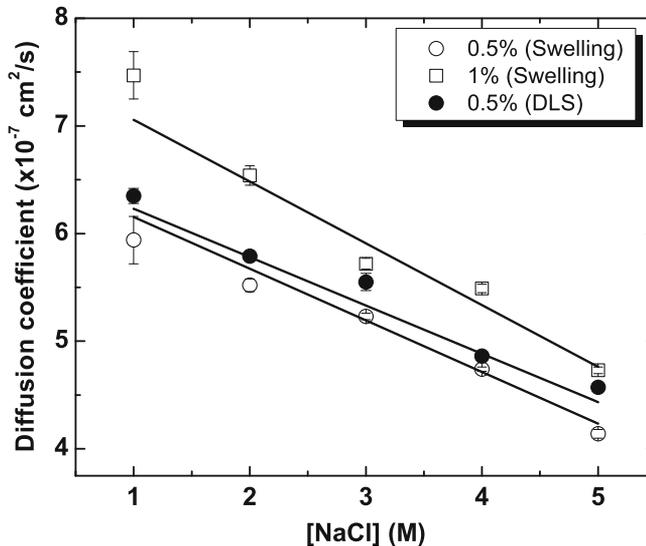$$f(q, t) = \exp\{-q^2\delta^2[1 - \exp(-(t/\tau)]\}, \tag{13}$$

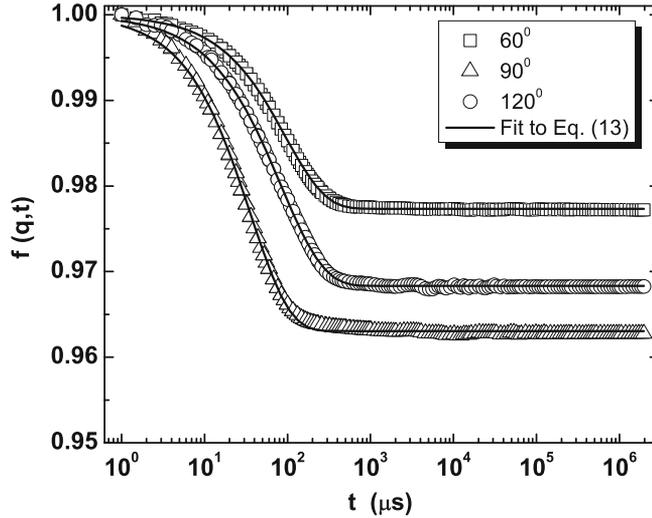**Figure 5.** Collective diffusion coefficient D vs. [NaCl] during swelling. Lines are guides to the eye.

Figure 6. Dynamic structure factor $f(q, t)$ of SSG (5 M NaCl) with 0.5% MBA at different scattering angles $\theta = 60°$, $90°$ and $120°$.

where δ^2 is the mean squared displacement of harmonically bound scatter at long times and τ is the relaxation time. Experimental data show a good fit to the above equation and τ is found to vary linearly with q^2 implying that initially the scatterers move diffusively. The collective diffusion coefficient $D = 1/(\tau q^2)$ obtained for 0.5% SSGs for different concentrations of NaCl are shown in figure 5. Notice that D obtained from DLS studies shows close agreement with those measured from macroscopic swelling studies and the same decreasing trend with increase in [NaCl].

   Static inhomogeneities are known to exist in a hydrogel network [29] and contribute to the non-fluctuating component of the scattered intensity in DLS signal. These inhomogeneities can also contribute to the non-decay of $f(q, t)$. These inhomogeneities swell (deswell) when polymer network undergoes swelling (deswelling) in the solvent. We show here that the comparison of SLS and DLS data on WSG and SSG gels enables one to extract information about changes in the polymer network as well as the size of the inhomogeneities. Figures 7 and 8 show respectively $f(q, t)$ vs. t and $\langle I(q) \rangle_E$ vs. q for WSG and SSG (5 M NaCl) with 0.5% MBA. The decay time, τ, and root-mean-square-displacement, δ, obtained by fitting $f(q, t)$ to eq. (13) are 61.7 μs, 15.7 nm and 83.9 μs, 9.9 nm for WSG and SSG (5 M NaCl) respectively. In HBBP model, the particles (scatterers) that constitute the gel network are bound in the network. These scatterers with radius a diffuse initially as free particles but cannot diffuse infinitely as they encounter restoring force by the network. The effective spring constant C of the network and the particle size a can be determined by knowing τ and δ^2 through the relations $C = k_B T/\delta^2$ and $\tau = 6\pi \eta a/C$. We found C and a to be 1.7×10^{-5} N/m, 61 nm and 4.2×10^{-5} N/m, 209 nm for WSG and SSG (5 M NaCl), respectively. The ensemble-averaged scattered intensity $\langle I(q) \rangle_E$ (figure 8) is higher for all values of q for SSG (5 M NaCl) compared to WSG because of the increase in a from 61 to 209 nm (shown schematically in figure 9). Further, it can be seen in figure 9 that the scattered intensity at low q-region is higher when
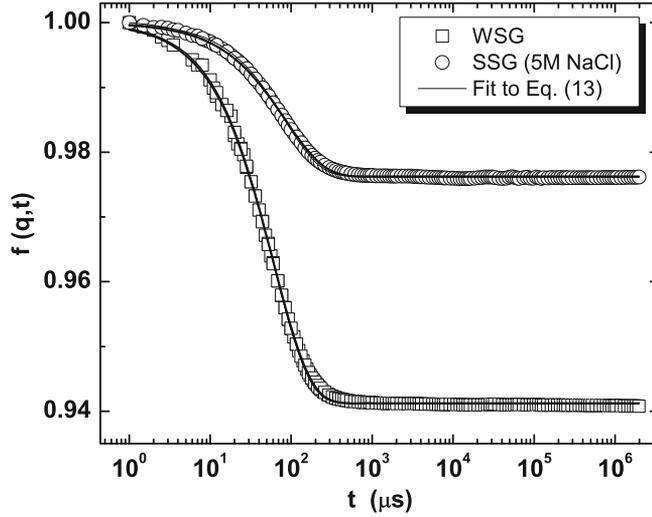
Figure 7. Dynamic structure factor $f(q, t)$ of WSG and SSG (5 M NaCl) with 0.5% MBA at $\theta = 60°$.

compared to the high q-region for both WSG and SSG (5 M NaCl). This observation clearly indicates the presence of inhomogeneities (shown schematically in figure 9). The size of inhomogeneities is determined by fitting the scattering profiles to the following expression [30] consisting of Gaussian and Lorentzian terms:

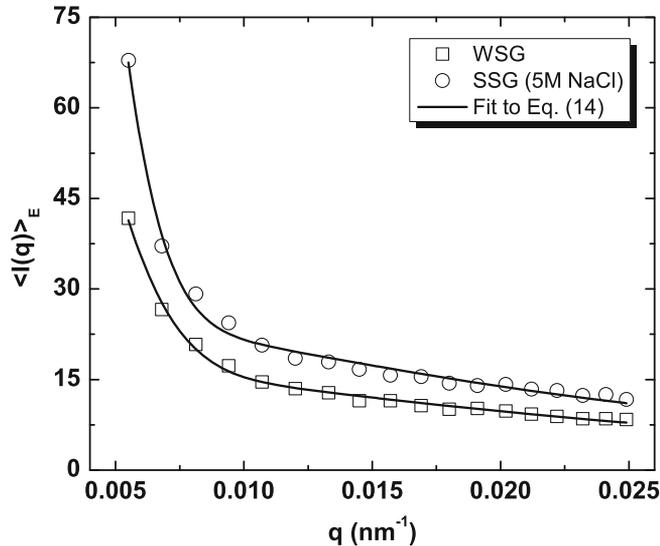$$I_s(q) = I_G(0) \exp(-\Xi^2 q^2/2) + I_L(0)/(1 + \xi^2 q^2). \tag{14}$$

Figure 8. Ensemble-averaged scattered intensity, $\langle I(q) \rangle_E$, of WSG and SSG (5 M NaCl) with 0.5% MBA.
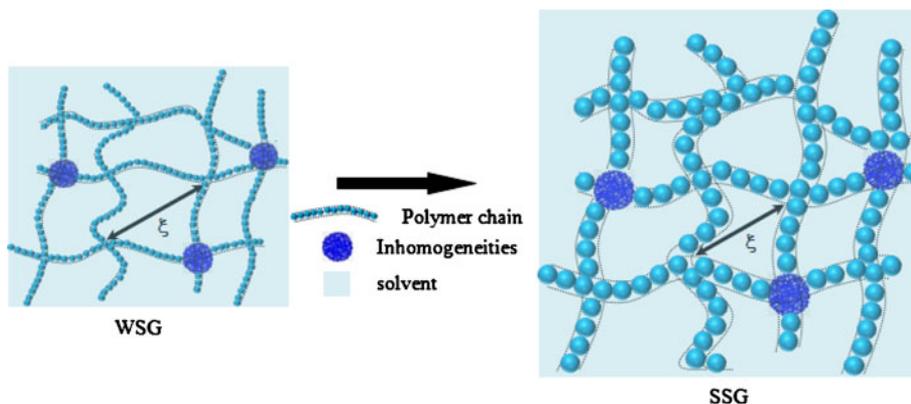
Figure 9. Schematic of the influence of concentrated NaCl solution on the swelling of WSG.

Here, $I_G(0)$ and $I_L(0)$ are coefficients of the Gaussian and Lorentzian terms, Ξ is the size of inhomogeneities and ξ is the correlation length. From the fit, we found that the size of the inhomogeneities increases from 296 nm to 337 nm when the WSG is transferred from water to 5 M NaCl whereas ξ is found to decrease slightly from 40 nm to 37 nm. These findings obtained by analysing the SLS and DLS data on WSG and SSG are schematically shown in figure 9. Further, we also understand that the linear decrease of D with increase in [NaCl] (figure 6) is due to the increase in particle size a and our observations support the earlier reports [31,32] that PAAm macrogel is formed from interconnected microgels (particles) along with inhomogeneities and the size of the inhomogeneities as well as particle size increase upon swelling in NaCl solutions.

4. Conclusions

Swelling (deswelling) behaviour of WSG (SSG) in NaCl solution (deionized water) was respectively investigated by macroscopic swelling measurements as well as by light scattering techniques. Several parameters such as bulk modulus K, polymer–solvent interaction parameter χ and collective diffusion coefficient D, characterizing the PAAm hydrogel network are determined. The decrease in χ with increase in NaCl concentration suggests that PAAm hydrogel swells in NaCl solutions due to the decrease in polymer–polymer affinity. HBBP model is found to describe the dynamics in PAAm hydrogels. Comparison of static and dynamic light measurements on WSG and SSG has revealed the presence of inhomogeneities and allowed us to determine the size of inhomogeneities as well as the size of the particles that constitute the gel network. The increased size of the particles with increase in salt concentration is responsible for the decrease in collective diffusion coefficient. Present studies have clearly revealed that salt solutions of higher concentration have strong influence on the swelling and deswelling properties of neutral polymer hydrogels.

Acknowledgements

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