



**Screening lengths and osmotic compressibility of flexible polyelectrolytes in excess salt solutions**

Journal:	<i>Soft Matter</i>
Manuscript ID	SM-ART-03-2020-000464.R3
Article Type:	Paper
Date Submitted by the Author:	30-Jun-2020
Complete List of Authors:	Gonzalez Lopez, Carlos; Rheinisch Westfalische Technische Hochschule Aachen, Physical Chemistry Horkay, Ferenc; National Institute of Child Health and Human Development, Section on Quantitative Imaging and Tissue Sciences Mussel, Matan; National Institute of Child Health and Human Development, Jones, Ronald; NIST, Polymers Division Richtering, Walter; RWTH Aachen University, Institute of Physical Chemistry

# Screening lengths and osmotic compressibility of flexible polyelectrolytes in excess salt solutions

Carlos G. Lopez,<sup>1, a)</sup> Ferenc Horkay,<sup>2, b)</sup> Matan Mussel,<sup>2)</sup> Ronald L. Jones,<sup>3)</sup> and Walter Richtering<sup>1)</sup>

<sup>1)</sup>*Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany*

<sup>2)</sup>*Section on Quantitative Imaging and Tissue Sciences, Eunice Kennedy Shriver National Institute of Child Health and Human Development, National Institutes of Health, 49 Convent Drive, Bethesda, MD 20892, USA*

<sup>3)</sup>*Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*

a) [lopez@pc.rwth-aachen.de](mailto:lopez@pc.rwth-aachen.de)

b) [horkayf@mail.nih.gov](mailto:horkayf@mail.nih.gov)

## ABSTRACT

We report results of small angle neutron scattering measurements made on sodium polystyrene sulfonate in aqueous salt solutions. The correlation length ( $\xi$ ) and osmotic compressibility are measured as a function of polymer ( $c$ ) and added salt ( $c_S$ ) concentrations, and the results are compared with scaling predictions and the random-phase approximation (RPA). In Dobrynin et al's scaling model the osmotic pressure consists of a counter-ion contribution and a polymer contribution. The polymer contribution is found to be two orders of magnitude smaller than expected from the scaling model, in agreement with earlier observations made on neutral polymers in good solvent condition. RPA allows the determination of single-chain dimensions in semidilute solutions at high polymer and added salt concentrations, but fails for  $c_S \leq 2M$ . The  $\chi$  parameter can be modelled as the sum of an intrinsic contribution ( $\chi_0$ ) and an electrostatic term:  $\chi \sim \chi_0 + K'/\sqrt{c_S}$ , where  $\chi_0 > 0.5$  is consistent with the hydrophobic nature of the backbone of NaPSS. The dependence of  $\chi_{elec} \sim 1/\sqrt{c_S}$  disagrees with the random-phase approximation ( $\chi_{elec} \sim 1/c_S$ ), but agrees with the light scattering results in dilute solution and Dobrynin et al's scaling treatment of electrostatic excluded volume.

## I. INTRODUCTION

The effect of counterions on the conformation and structure of polyelectrolytes in solution has attracted a great deal of interest because of its importance in many biological processes such as DNA condensation<sup>1</sup>, protein folding<sup>2</sup> or joint lubrication<sup>3-4</sup>. An understanding of the mechanisms that determine the conformation of charged macromolecules is required to tailor the properties of novel functional materials, including pharmaceutical<sup>5-6</sup> and food products<sup>7-8</sup>. It has been found that changes induced by monovalent salts can be described by the Poisson-Boltzmann model despite its serious limitations arising from its the mean-field nature.<sup>9-15</sup> For example, the Boltzmann distribution does not account for the finite size of ions and the size dependent ion-ion correlations and fluctuation contribution to the ion distributions. In certain systems, specific interactions between the polymer chains and the ions may also play a significant role, which introduces further complexities that make the interpretation of the experimental results more difficult.<sup>16-20</sup>

In semidilute polymer solutions, i.e. above the overlap concentration, polymer chains interpenetrate forming networks with a concentration dependent mesh size  $\xi$ , known as the correlation length<sup>21</sup>. The correlation length governs the thermodynamic, conformational and hydrodynamic properties of polymer solutions and gels.<sup>21-33</sup> The concentration and solvent quality dependence of  $\xi$  in semidilute and concentrated solutions of neutral polymers has been

extensively studied, and interpreted by mean-field and scaling theories<sup>21,23-25</sup>. Polyelectrolytes in salt-free solution display markedly different behavior from those of neutral polymers<sup>26-29</sup>. Owing to strong electrostatic repulsion along the backbone, they adopt highly extended conformations and their scattering function displays a correlation peak. Traditional liquid state theories such as the mean spherical approximation or the random approximation show limited success in describing the properties of salt-free polyelectrolytes due to the strong correlations between chains.<sup>34</sup> More recent works by Jiang et al and von Solms and co-workers based on the mean spherical approximation and hypernetted chain closures to the Ornstein-Zernike equations give more accurate results, but the calculation methods are rather involved and mapping analytical calculations to experimental data requires unrealistic values for the monomer volume of vinylic polyelectrolytes<sup>35-39</sup>. PRISM theories, which have been applied extensively to polyelectrolytes by Yethiraj and co-workers give a more accurate description of the conformational and thermodynamic properties of polyelectrolytes in salt-free and excess salt solutions, and can reproduce many of their scattering properties.<sup>34,40,41</sup>

Structural and thermodynamic features of polyelectrolyte solutions have been successfully reproduced by simulations<sup>14,15,42-50</sup>, including the concentration dependence of the scattering peak in the dilute and semidilute regimes<sup>51,52</sup>, or the low- $q$  upturn<sup>47-48</sup>. Simulations by Dobrynin and co-workers are in good agreement with Dobrynin et al's scaling predictions for the chain size and osmotic pressure of polyelectrolyte solutions<sup>53-56,57</sup>. More recently, simulations of Chang et al<sup>58</sup> have suggested that the polymer contribution to the osmotic pressure of polyelectrolyte solutions exceeds that expected from Dobrynin et al's scaling model.

A transition from highly extended rod-like conformation in salt-free solutions to expanded coils in excess salt has been observed for various systems in dilute solution<sup>33,59-61</sup>. Studies on the scattering properties of semidilute polyelectrolyte solutions with excess added salt are sparse, with most earlier literature focusing either on single chain properties<sup>62-63</sup> or on the influence of specifically interacting multivalent counterions<sup>64-65</sup>. It is frequently assumed that polyelectrolytes in large excess of added salt behave like neutral polymers. When the concentration of added ions is sufficiently high, the electrostatic interaction between the charged groups is largely screened, resulting in a polymer that is essentially neutral with only weak effective electrostatic interactions. Extensive studies by Norisuye and co-workers have shown that the conformational (chain size) and transport (diffusion coefficient, intrinsic viscosity) properties of polyelectrolytes in dilute solutions containing excess added salt are similar to those of neutral polymers in good solvent.<sup>66-70</sup> The persistence length and excluded volume strength of various polyelectrolytes have been shown to decrease with increasing ionic strength.<sup>29,66-70</sup> At sufficiently high salt concentrations, the chemical details of the chain become important, and hydrophobicity and specific ion effects lead to a decrease of the solvation of the polymer backbone. Such effects are difficult to treat theoretically.

In the present work, the small angle neutron scattering (SANS) response of sodium polystyrene sulfonate (NaPSS) solutions containing large excess of monovalent counterions has been systematically investigated in the semidilute concentration regime. NaPSS is a well-suited model polymer to investigate ion-polymer interactions, particularly the effect of sodium counterions on the electrostatic interactions and molecular conformation, because no specific interactions between NaPSS and sodium ions have been reported in aqueous solutions.

We report experimental results for the correlation length and osmotic compressibility of

NaPSS solutions as a function of the added salt concentration, primarily focusing on the excess added salt-regime. It is found that the results disagree with the predictions of the scaling theory. It is also demonstrated that the behaviour of charged polymers in solutions at high salt concentrations exhibit significant differences from that of neutral polymers.

The paper is organized as follows. The theoretical section is followed by a brief description of the materials and methods. Then we present the results of SANS measurements analyzed in terms of the Ornstein-Zernike equation. The influence of the polymer concentration and monovalent ions (sodium chloride) concentration is studied in semidilute NaPSS solutions.

### III. THEORY

Using simple scaling arguments, de Gennes derived the concentration dependence of  $\xi$  of polymer solutions<sup>22</sup>:

$$\xi \approx R(c^*) \left(\frac{c}{c^*}\right)^\gamma \approx \begin{cases} Ac^{-0.77} & \text{good solvent} \\ Ac^{-1} & \theta - \text{solvent} \end{cases} \quad (1)$$

where  $c$  is the polymer concentration (number of repeating units per unit volume),  $R$  is the end-to-end distance of the polymer chain,  $c^*$  is the overlap concentration, and  $A$  is a constant depending on the monomer size, Kuhn length and thermal blob size. Equation 1 has been found to be in agreement with experimental data for the correlation length of neutral polymers, particularly under good solvent conditions [see 22,23,71-73]. Scaling theory predicts that correlation blobs repel each other with an energy  $kT$ , where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The polymer contribution to the osmotic pressure ( $\Pi_p$ ) is:

$$\Pi_p \approx kT\xi_{II}^{-3} \quad (2)$$

which describes the concentration dependence of  $\Pi$  of neutral polymers both in good and  $\theta$  solvents. [We use the subscript  $II$  to distinguish the correlation length obtained from the osmotic pressure from that determined from scattering measurements  $\xi_{OZ}$ , (see Eq. 9).] For neutral polymers,  $\xi_{II}$  is proportional to and larger than  $\xi_{OZ}$ , with the proportionality constant increasing with increasing solvent quality.<sup>22,23</sup>

The correlation length of polyelectrolyte solutions depends on the polymer and added salt concentrations. Dobrynin's scaling model predicts<sup>53</sup>:

$$\xi(c_s) = \xi(0)[1 + 2c_s/(fc)]^{1/4} \quad (3)$$

where  $\xi(0) \equiv \xi_{SF} = (b')^{3/2}c^{-1/2}$  is the correlation length in salt-free solution,  $b' = b/B$  is the effective monomer length, with  $b$  the chemical monomer size and  $B$  the stretching parameter<sup>29,53</sup>,  $c_s$  is the added salt concentration and  $f$  is the degree of dissociated counterions. For  $c_s \gg fc$ , Eq. 3 has the form  $\xi \propto c_s^{1/4}c^{-3/4}$ .

The osmotic pressure of polyelectrolyte solutions contains a contribution analogous to that of neutral polymers in good solvent ( $kT\xi^{-3}$ ) and a term arising from counterion osmotic pressure, which may be approximated as<sup>53</sup>:

$$\Pi_i \approx kT \frac{c^2}{4c_s/f^2 + c/f}$$

see refs. [54-58,71,74-75] for a discussion of the validity of this term. The osmotic compressibility arising from the polymer and counterions for solutions in excess added salt can, therefore, be given as:

$$\frac{d\Pi_p}{dc} = kT \frac{3\gamma}{A_{\Pi}^3} c^{-(3\gamma+1)} \quad (4a)$$

$$\frac{d\Pi_i}{dc} = kT \frac{f^2 c}{2c_s} \quad (4b)$$

where  $\xi_{\Pi} = A_{\Pi} c^{\gamma}$  and  $4c_s/f \gg c$ .<sup>76-80</sup> The scaling exponent predicted by Eq. 4a has been shown to apply for several neutral polymer-solvent systems of varying solvent quality<sup>21,72-73</sup>, as well as biological polyelectrolytes in excess added salt<sup>28</sup>.

The structure factor at zero scattering wave-vector  $q$  is:

$$S(0) = kT\phi \frac{d\phi}{d\Pi} \quad (5)$$

where  $\phi$  is the volume fraction and  $d\phi/d\Pi$  is the inverse osmotic compressibility. For neutral polymers in good solvent (excluded volume exponent  $\nu = 0.59$ ) scaling theory predicts  $\xi \propto c^{-0.77}$ ,  $\Pi \propto c^{2.3}$  and  $S(0)/c \propto c^{-0.31}$ , which matches the experimental data, see refs [21, 23-25,72,73, 81-87]. However, the correlation length obtained from scattering and osmotic pressure measurements differs by a factor of  $\approx 4$ , which is not anticipated from the scaling theory. At high polymer concentrations,  $\xi$  decreases to values well below the Kuhn length ( $l_K$ ) of neutral polymers, which is incompatible with the scaling interpretation of the correlation length.<sup>24,88</sup>

In many experiments made on neutral polymers the structure factor of the polymer solution has been modeled by the random phase approximation (RPA) expression:

$$\frac{1}{S(q)} = \frac{1}{\phi N v_p P(q)} + \frac{1}{(1-\phi)v_s} - \frac{2\chi}{v_s} \quad (6)$$

where  $v_s$  and  $v_p$  are the volumes of the solvent and monomer molecules, respectively,  $\phi$  is the volume fraction of the polymer and  $P(q)$  is the polymer form factor, normalized to  $P(0) = 1$ , and  $\chi$  provides a measure of the polymer-solvent interaction. For  $1/R_g < q < 1/\xi$ , the form factor can be approximated as  $P(q) \approx 2/(qR_g)^2$ , where  $R_g$  is the radius of gyration. Equation 6 then gives:

$$\frac{1}{S(q)} = \left[ \frac{R_g^2}{2\phi N v_p} \right] q^2 + \frac{1}{(1-\phi)v_s} - \frac{2\chi}{v_s} \quad (7)$$

In the range  $1/\xi < q < 1/l_K$ , the form factor depends on the solvent quality  $P(q) \propto (qR_g)^{1/\nu}$ , and Eq. 7 takes a similar form but with the term in square brackets being multiplied by  $q^{1.7}$  instead of  $q^2$ . For semidilute solutions, where excluded volume interactions are screened beyond the correlation length,  $R_g^2/N$  does not depend on  $N$  and Eq. 6 predicts  $I(q)$  to be independent of the polymer molar mass, a feature that agrees with experimental observations of neutral polymers.

The random phase approximation method was applied to weakly and strongly charged polyelectrolytes by Vilgis and Borsali<sup>89-90</sup>, yielding expressions, which in the excess salt limit become analogous to Eqs. 6-7, with a  $\chi$  parameter that depends on  $c_s$ . Muthukumar's double screening theory<sup>91</sup> makes a similar prediction for flexible polyelectrolytes in the presence of excess added salt.

In the present paper, we interpret the polyelectrolyte solution data by eq. 6 understanding that this equation is only appropriate for high salt concentrations, where polyelectrolyte chain aggregation is suppressed. For polyelectrolytes in excess salt solution, the  $\chi$  parameter contains an intrinsic contribution ( $\chi_0$ ), which reflects the polymer solvent interactions in the absence of Coulombic forces, and an electrostatic contribution, which we consider in more detail in the Discussion section.

## II. EXPERIMENTAL

Materials: Sodium styrene sulfonate (NaSS), sodium chloride and D<sub>2</sub>O were purchased from Sigma-Aldrich. Potassium persulfate (KPS) was purchased from VWR.<sup>92</sup> De-ionised (DI) water was obtained from a milli-Q source. Dialysis membranes were purchased from Spectra-Por. (The identification of commercial products does not imply endorsement by the National Institute of Standards and Technology nor does it imply that these are the best for the purpose.)

Preparation of sodium polystyrene sulfonate: NaPSS was synthesized by free-radical polymerization of (NaSS) in aqueous media using KPS as an initiator. 70 mL of water was degassed for one hour and heated to 50 °C in a round bottomed flask. An aqueous solution of KPS was added and stirring was continued until it was fully mixed. The reaction was allowed to proceed for five hours, with nitrogen being bubbled continuously. The solution was cooled down and the polymer was precipitated by addition of fourfold methanol and excess NaCl. The polymer was then washed in methanol and re-dissolved in water. Solutions were extensively dialyzed against DI water to remove any residual salt and then freeze dried. This method is expected to yield 100% sulfonation. Five other NaPSS polymers synthesised by sulfonation of polystyrene standards were purchased from Polymer Standard Services (Mainz, Germany). The molar mass of these samples varies between 258 kg/mol and 2000 kg/mol, and the sulfonation degree is estimated by the manufacturer to be  $\approx 95\%$  and the polydispersity is  $pd \approx 1.1$ . Solutions from the dried polymer were prepared gravimetrically by assuming a polymer density of 1.65 g/mL.

Small Angle Neutron Scattering: SANS experiments were performed at the NGB 30m and NGB 10m Small Angle Neutron Scattering instruments at the NIST Center for Neutron Research (Gaithersburg, MD, USA) and the D11 beamline at the ILL. We employed sample-to-detector distances of 1.3 m, 4 m and 13.4 m and 1.5m, 4.5m and 13m (NGB 30m,  $\lambda = 6\text{\AA}$ ), 1.5 and 8m (D11,  $\lambda = 6\text{\AA}$ ) and 1.55 m and 5 m (NGB 10m,  $\lambda = 5\text{\AA}$ ). More details on instrument configuration are given in the supporting information. An empty cell reading was subtracted from the samples. Absolute calibration was made against a direct beam, according to NIST standard procedures. Samples were measured in Hellma cells of the QS series.

## III. RESULTS AND DATA ANALYSIS

Figure 1 shows the background subtracted SANS profiles of NaPSS solutions measured at different polymer concentrations at constant salt concentration (part a) and at different salt concentrations at constant polymer concentration (part b).

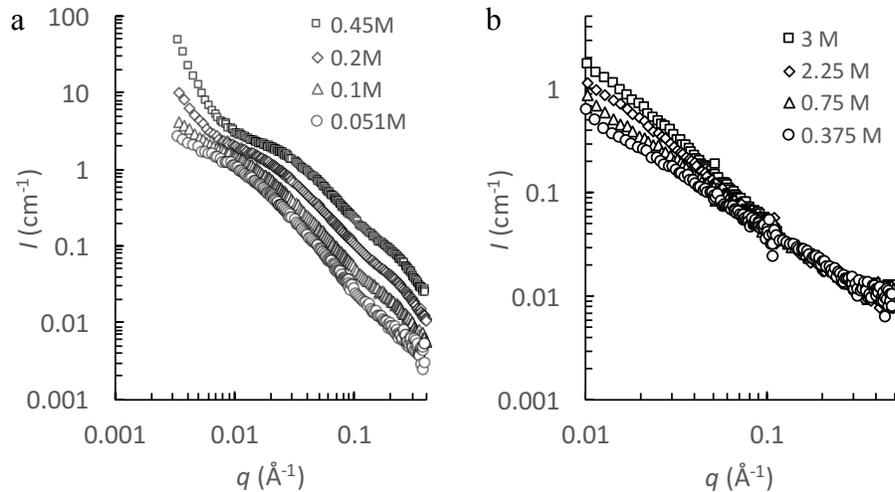


FIGURE. 1. Background subtracted scattering intensity for NaPSS in aqueous NaCl solutions. a:  $c_s = 3$  M, polymer concentrations are indicated in the figure. The lowest two concentration solutions were filtered ( $0.2 \mu\text{m}$ ) prior to measurement. Measurements made by the NGB 30m instrument. b:  $c = 0.1$  M, salt concentrations are indicated in the figure. Measurements made by the NGB 10m instrument.

The scattering intensity relates to the structure factor as:

$$I(q) = \left[ \frac{b_m}{v_m} - \frac{b_s}{v_s} \right]^2 S(q) \quad (8)$$

where  $b$  and  $v$  are the scattering length and volume, respectively, and the subscripts m and s refer to the monomer and solvent. In Eq. 8 the scattering arising from salt is neglected.

In analogy to neutral polymers, the scattering of a polyelectrolyte solution in excess added salt can be described by a Lorentzian function:

$$1/I(q) = A + Bq^2 \quad (9)$$

where  $A$  and  $B$  are fit parameters, related to the zero angle scattering intensity and correlation length as  $I(0) = 1/A$  and  $\xi_{OZ} = B/A$ . We use the subscript OZ to denote that the correlation length was obtained by fitting the Ornstein-Zernike expression.

The osmotic correlation length  $\xi_{II}$  is obtained from the experimentally determined values of  $I(0)$  and Eqs. 4, 5 and 8, see the supporting information for more details.

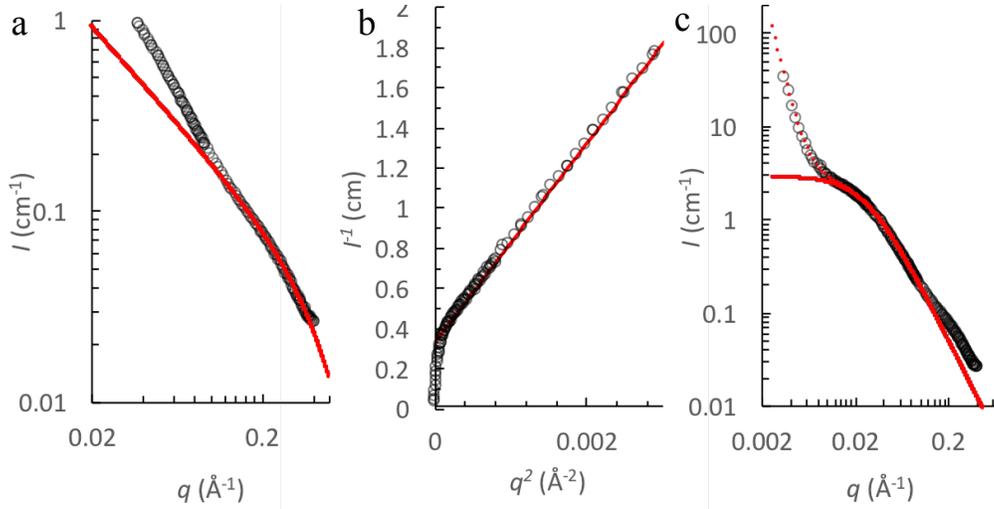


FIGURE. 2. Fitting procedure to determine the correlation length and zero-scattering intensity. Circles: coherent scattering intensity for sample with  $c = 0.38$  M,  $c_s = 3$  M. a: Fit to worm-like chain form factor at high  $q$ , red line is  $P(q) = \pi/(b'q)e^{-q^2R_c^2/4}$ . b: Fit to Lorentzian function (first term of Eq. 9). c: Fit to Eq. 9 with clustering term (dotted line) and to Lorentzian term only (full line).

The fitting procedure to estimate the background (including incoherent and other  $q$ -independent scattering contributions), correlation length and clustering term is illustrated in Figure 2. The high  $q$  region is fitted to a worm-like chain form factor in the  $qL_K > 1$  limit:  $S(q) \approx P(q) = \pi/(b'q)e^{-q^2R_c^2/4} + Bkgd$ , where  $b'$  is the effective monomer length<sup>23,53</sup>,  $R_c$  is the cross-sectional radius of the chain (set to  $0.4$  nm<sup>93</sup>) and  $Bkgd$  is a constant that accounts for the  $q$ -independent scattering contribution. A representative fit to this equation is shown in Fig. 2a. The correlation length is estimated by fitting the Ornstein-Zernike function (Eq. 9) in the mid- $q$  region, as illustrated in Fig. 2b. Finally, a power-law term  $I(q) = Dq^{-m}$ , where  $D$  and  $m$  are constants, is added to account for the excess scattering at low- $q$ , see Fig 2c.

## V. DISCUSSION

Figure 3a and 3b show the correlation length and reduced zero angle scattering intensity respectively as a function of polymer concentration in solutions of different salt contents for the NaPSS synthesised by polymerisation of styrene sulfonate. Data for samples obtained by sulfonation of polystyrene are shown in the supporting information and yield similar results. No effect of the polymer molar mass on  $\xi$  or  $I(0)$  is observed, as expected for semidilute solutions. Both  $\xi$  and  $I(0)$  decrease as power-laws of the polymer concentration at constant salt concentration, as shown by the best-fit lines. The increase of the correlation length and of the zero-angle scattering intensity with increasing content of added salt is consistent with a decrease in solvent quality, which leads to concentration fluctuations occurring on larger length-scales.

### A. Scaling Analysis

The scaling model predicts that  $\xi$  and  $I(0)$  are related through Eqs. 2, 4 and 5. Applying

these equations, we find that the calculated values of  $I(0)$  are nearly two orders of magnitude smaller than the measured ones. This discrepancy indicates that  $\xi_{OZ} < \xi_{\Pi}$ , which has been reported for several neutral polymer systems<sup>24,25</sup>.

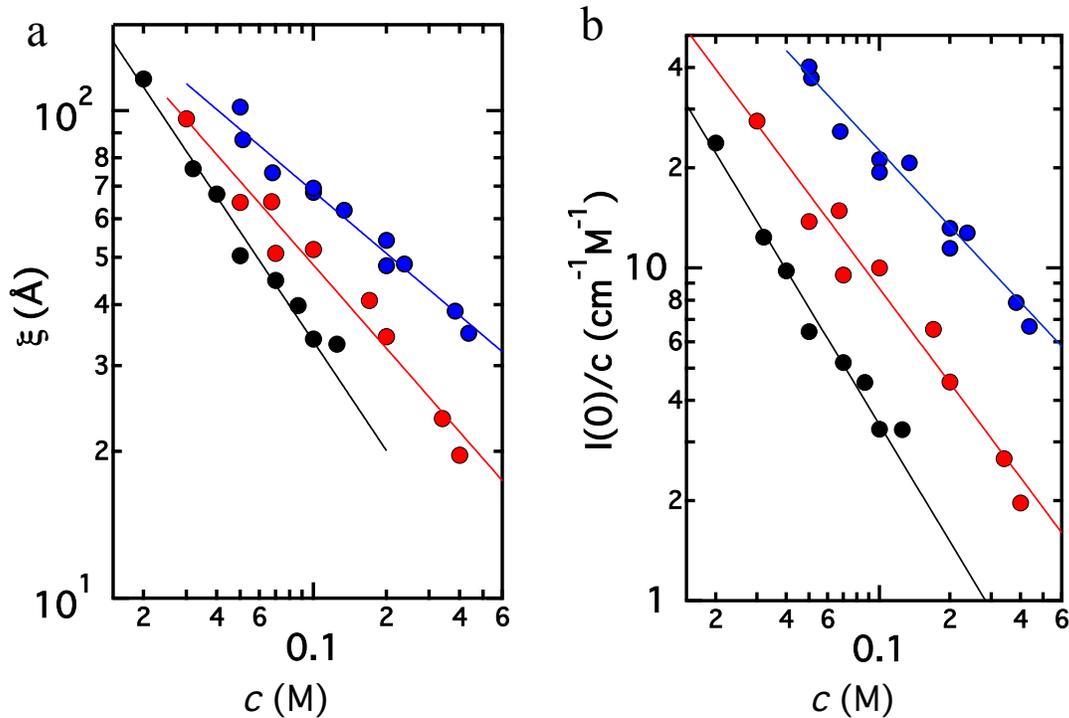


FIGURE. 3. Correlation length (a) and reduced zero angle scattering intensity (b) as a function of the polymer concentration at different concentrations of added salt. Symbols:  $c_s = 3$  M (blue), 1.5 M (red) and 0.375 M (black).

Figure 4a plots the ratio  $\xi_{\Pi}/\xi_{OZ}$  required to match the measured and calculated osmotic compressibilities as a function of the added salt concentration, (see supporting information for more details). At high  $c_s$ ,  $\xi_{\Pi}/\xi_{OZ} \approx 4.2$  is found, which is close to the value 3.8 reported for neutral polymers in good solvent<sup>24,25</sup>, indicated by the dashed line in Fig 4a. The observed  $I(0)/c$  vs.  $c$  exponents and those calculated from Eqs. 4-5 are in reasonably good agreement (see Fig. 4b). The origin of the  $\xi_{\Pi}/\xi_{OZ} \approx 4.2$  factor is discussed below.

In Fig. 4c the exponent  $\gamma$  obtained from the concentration dependence of  $\xi$  ( $\propto c^\gamma$ ) is plotted as a function of  $c_s$ . For  $c_s = 0.375$  M, the data display the expected<sup>53</sup> scaling dependence of  $\xi \propto c^{-0.75}$ . For higher  $c_s$ , the concentration dependence becomes weaker, and matches experimental results obtained for flexible neutral polymers in good solvents such as polystyrene in dichloromethane or PDMS in toluene<sup>23,24</sup>. As  $c_s$  increases, the solutions approach the  $\theta$  point ( $\approx 4.17$  M NaCl at  $T \approx 290$  K<sup>94</sup>). Scaling theory predicts that  $\gamma$  should decrease from -0.77 at low added excess salt concentration (i.e.  $c_s \ll 4.17$  M,  $c_s \gg fc/2$ ) to  $\gamma = -1$  at the  $\theta$  state, a feature that has been observed in some neutral polymer systems in organic solvents (e.g. polystyrene/cyclohexane<sup>21,23</sup>) but not in aqueous environment<sup>95,96</sup>. In the present system the

exponent increases to  $\gamma \approx -0.45$  at  $c_s = 3$  M. This type of behaviour is similar to that observed for neutral polymers in aqueous solutions near the  $\theta$  point. To the best of our knowledge, two such systems have been previously studied: polyethylene oxide (PEO) in  $D_2O$  for  $T = 5-95$  °C<sup>95,96</sup> poly(isopropylacrylamide) (PNIPAM) solutions in  $D_2O$ <sup>73</sup> for  $T = 23-34$ °C. Shibayama and co-authors<sup>73</sup> attributed the deviation from the scaling theory to the dependence of the spinodal temperature ( $T_s$ ) on the polymer concentration. Experimental data obtained for polystyrene/cyclohexane system show a similar concentration dependence of  $T_s$ , but the  $\xi \approx c^{-1}$  dependence predicted by the scaling theory is observed.<sup>97</sup> Given that  $\gamma$  appears to be consistently lower in aqueous solution than in organic solvent, it is possible that hydrophobic interactions are responsible for the discrepancy.

The observed results for NaPSS upon increasing  $c_s$  are consistent with this trend: increasing the concentration of added salt decreases the excluded volume strength of the polymer and therefore has an analogous effect as that of the increasing temperature in the PEO/water or PNIPAM/water system. We note that it is well documented that in polyelectrolyte systems the polymer-solvent interaction parameter is strongly affected by the added salt.<sup>98</sup> At high salt content the hydrophobic forces between the hydrophobic groups on the polymer molecules dominate, and result in chain aggregation. This behavior is different from neutral polymer solutions, in which, at constant temperature and pressure, the thermodynamic interactions are defined by the polymer and the solvent molecules only. As discussed below, the experimental values of  $\chi$  and  $I(\theta)$  for NaPSS in excess added salt can be accounted for by the RPA method.

The measured  $\xi$  vs  $c$  exponents at the highest added salt concentrations differ appreciably from those observed for non-ionic polystyrene in good (toluene, 25 °C) or  $\theta$  (cyclohexane, 35 °C) solvent. However, the fact that the ratio of  $\xi_{II}/\xi_{OZ}$  is similar for sulfonated polystyrene in excess added salt ( $\xi_{II}/\xi_{OZ} \approx 4$ ) and non-sulfonated polystyrene in good solvent<sup>25,83,85</sup> ( $\xi_{II}/\xi_{OZ} \approx 3.8$ ) signals that the polymer contribution to the osmotic pressure is similar in both systems. The difference between the exponents may be the consequence of hydrophobic interactions.

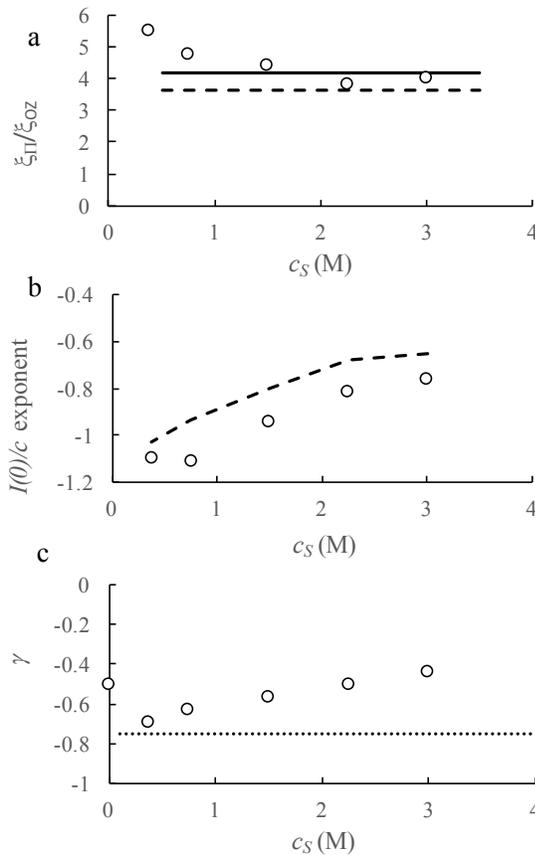


FIGURE. 4. a) Ratio of osmotic ( $\xi_{IT}$ ) and scattering ( $\xi_{OZ}$ ) correlation lengths. Full line: average value at high salt concentration, dashed line: value for neutral polymers in good solvent<sup>25</sup>. b) Exponent for the  $c$  dependence of  $I(0)/c$ . Data points are experimental values, dashed line shows the variation of the exponent calculated from Eqs. 2, 4 and 5. c) Exponent  $\gamma$ , which relates the polymer concentration and correlation length as  $\xi \propto c^\gamma$ . Dotted line is the scaling prediction for neutral polymers in good solvent and for polyelectrolytes in the presence of excess added salt.

The salt-dependence of the correlation length at constant polymer concentration is shown in Fig. 5a. The best fit exponents for  $c = 0.05, 0.1$  and  $0.2$  M, are  $0.28 \pm 0.07, 0.29 \pm 0.08$  and  $0.42 \pm 0.19$ , respectively. These values exceed the scaling prediction of 0.25 (see Eq. 3). In figure 5b  $\xi$  at fixed polymer concentrations is plotted as a function of  $[1 + 2c_S/fc]^{1/4}$ . According to Eq. 3 these plots should yield straight lines going through the origin, with a slope of  $\xi(0)$ . The first feature is approximately observed for data in excess salt, however, the slopes of the lines are smaller than expected from the correlation length values of polystyrene sulfonate in salt-free solution. The values of  $\xi$  in salt-free solution, calculated as  $\xi(c_S=0) = \xi_{peak} = 33c^{-1/2}$ , following earlier work<sup>29,99-101</sup>, are plotted as hollow symbols in Figure 5b. The salt-free values of the correlation length are 5 – 7 times larger than the values extrapolated from the excess salt data, depending on the polymer concentration. The scaling theory defines the correlation length as being equal to the end-to-end distance of a chain at the overlap concentration, i.e.  $\xi(c^*) = 6^{1/2}R_g(c^*)$  for Gaussian chains. On the other hand, comparison of Eq. 9 with the Zimm approximation yields  $\xi(c^*) \approx R_g/\sqrt{3}$ . The correlation lengths obtained from Eq. 9 are therefore

expected to be much smaller than  $\xi$  calculated by scaling. Adjusting the results of Eq. 9 by a factor of  $(3 \times 6)^{1/2} \approx 4.2$  would bring the excess-salt and salt-free data plotted in Fig 5b to better agreement, and would help explain the differences observed between  $\xi_{II}$  and  $\xi_{oz}$  both for NaPSS in excess added NaCl and for non-ionic polymers in good or  $\theta$  solvents.<sup>24,72</sup> An additional discussion on the length-scales at which excluded volume becomes screened is provided in section V.B.

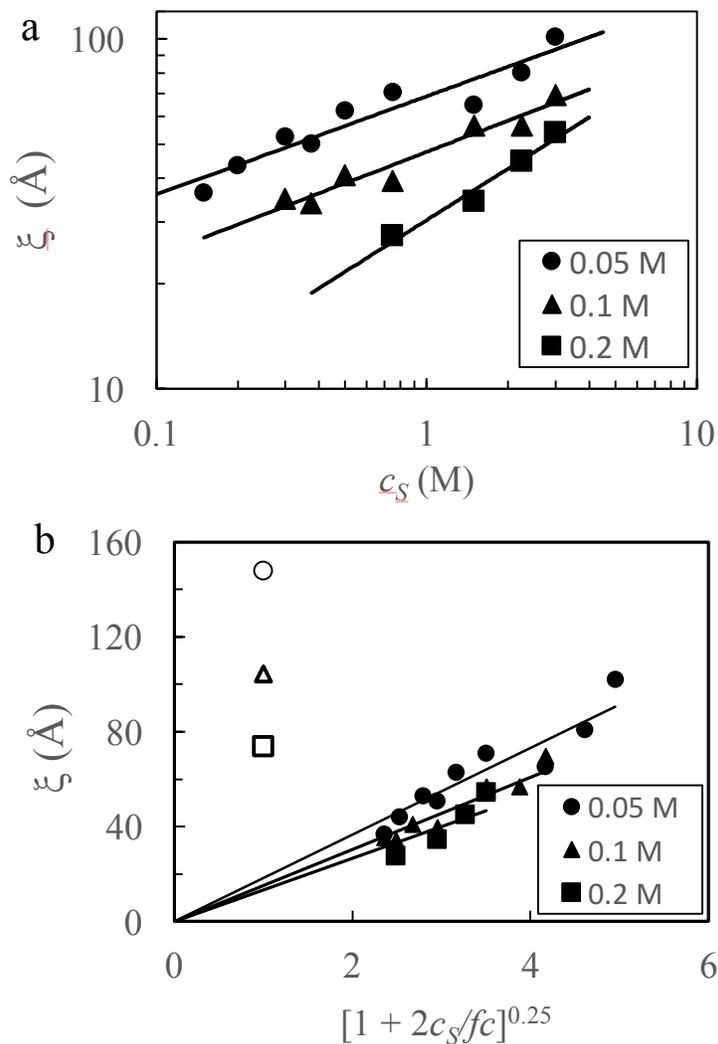


FIGURE. 5: Dependence of correlation length on the added salt concentration for different polymer concentrations, indicated on the legend. b: Scaling plot according to Eq. 3. Filled symbols are data measured in excess salt ( $\xi_{oz}$ ). Hollow symbols are for salt-free solutions, calculated from  $\xi_{peak} = 33c^{-1/2}$  Å.<sup>95,96</sup> Symbols have the same meaning in parts a and b.

## B. RPA and Double screening theory

Given the discrepancies between experimental data and the scaling theory, in particular

with respect to the dependence of the correlation length on the polymer concentration, we compare our experiments with the random phase approximation method, which is known to provide a reasonably good description of scattering from concentrated solutions of neutral flexible polymers.

### I. Chain dimensions

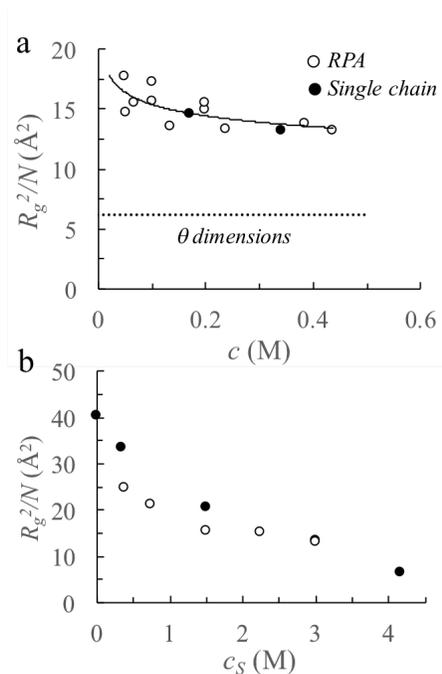


FIGURE. 6. a: Chain dimensions calculated from Eq. 7 (hollow symbols) and from single chain measurements by Spiteri<sup>102</sup> using the zero-average contrast method (filled symbols) as a function of polymer concentration in 3 M NaCl. The dashed line represents the  $\theta$  dimensions of the chain in 3M NaCl, see the text for details. b: same as part a) but plotted as a function of added salt concentration for  $c = 0.34$  M. The datum at  $c_s = 4.17$  M corresponds to NaPSS at the  $\theta$  condition  $17.8^\circ\text{C}$ .<sup>94</sup> All values calculated from Eq. 7 are for solutions in excess added salt.

The concentration dependence of  $R_g$  in salt-free solution is discussed extensively in ref 29 and shown to be in agreement with the scaling theory of Dobrynin et al<sup>53</sup> and Muthukumar's double screening theory.<sup>91</sup> Figures 6a and 6b compare the values of  $R_g^2/N$  in excess salt calculated from Eq. 7 and our data with direct measurements by Spiteri<sup>102</sup> using the zero-average contrast (ZAC) method as a function of polymer and added salt concentrations, respectively. Spiteri estimated  $R_g$  from the slope of the form factor at low- $q$ , using the Zimm approximation.<sup>102</sup> For  $c_s = 3$  M, good agreement is found between the two methods. For lower added salt concentrations, the RPA consistently underestimates the dimensions of NaPSS chains. The level of disagreement between the two estimates is similar to that observed by Graessley for neutral polymers in good and  $\theta$  solvents.<sup>24</sup>

Semidilute solution data from this study and Spiteri's may be compared with Norisuye and co-workers' measurement in dilute solution<sup>66,69,94,103</sup>. At  $c_s = 3$  M, the unperturbed (i.e. theta)

dimensions of NaPSS are calculated as  $R_g^2/N = (LL_K)/6N$  using Norisuye and co-worker's estimates for the Kuhn length and mass per unit length of  $L_K = 15 \text{ \AA}$  and  $M_L = 880 \text{ g/mol/nm}$ . This gives a value of  $R_g^2/N = 5.5 \text{ \AA}^2$ , which is significantly lower than our estimates based on the RPA method and Spiteri's direct measurements  $R_g^2/N \approx 12 \text{ \AA}^2$  at  $c \approx 0.4 \text{ M}$ , see the supporting information for further discussion of this.

## II. Correlation length and zero-angle scattering intensity

Muthukumar's double screening theory<sup>91</sup> predicts  $\xi \sim c^{-1/2}$  at low added salt concentrations,  $\xi \sim c^{-3/4}$  at high salt and moderate polymer concentrations, and  $\xi \sim c^{-1/2}$  for concentrated polyelectrolyte solutions in the presence of excess salt. The RPA (Eq. 7) also expects  $\xi \sim c^{-1/2}$  and  $I(0)/c \sim c^{-1}$  in excess salt if  $R_g^2/N$  and  $I/(1 - \phi) - 2\chi$  do not vary appreciably with the polymer concentration. The observed dependences for NaPSS in 3 M NaCl deviate from this prediction by 20-30%, which may be attributed to a concentration dependence of the  $\chi$  parameter and a decrease of  $R_g^2/N$  with concentration. The zero-angle scattering intensity, plotted for selected added salt concentrations in Figure 3b, may be expressed in terms of the  $\chi$  parameter using Eq. 6. The RPA method and Muthukumar's double screening theory predict:

$$\chi = \chi_0 - \frac{K}{c_S} \quad (10)$$

where  $K$  is a constant, that depends on the relative permittivity of the solvent and the Kuhn length of the polymer.<sup>91</sup>

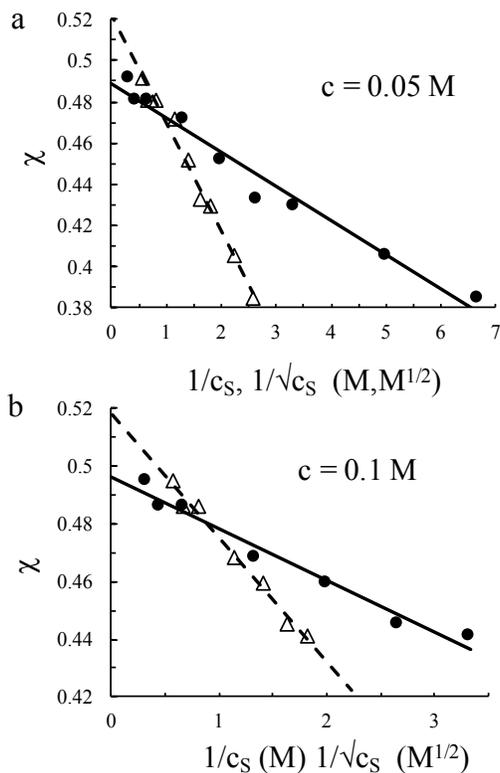


FIGURE. 7. The polymer-solvent interaction parameter  $\chi$  as a function of  $1/c_S$  (full circles) and  $1/\sqrt{c_S}$  (open triangles) for  $c = 0.05$  M (a) and  $c = 0.1$  M (b). Lines are the best linear fits to the data, see table 1.

In Figure 7 the  $\chi$  parameter is plotted as a function of  $1/c_S$  for  $c = 0.05$  and  $0.1$  M. The linear relation predicted by Eq. 10 is observed for all polymer concentrations studied. The  $1/c_S = 0$  intercept yields  $\chi_0 \approx 0.49$ , which appears too low given the hydrophobic nature of the polystyrene backbone. Assuming instead a dependence of

$$\chi = \chi_0' - K'/c_S^{1/2} \quad (11)$$

gives a more reasonable estimate  $\chi_0' \approx 0.52$ . The various  $\chi_0$  and  $K$  values obtained from fits at different concentrations are listed in Table 1. No clear trends are discernible for  $K$  or  $K'$  due to the relatively large experimental errors. At the infinite-salt limit  $\chi$  appears to show a weak increase with polymer concentration, in accordance with findings for neutral polymer solutions and gels<sup>24,74,75</sup>. The level of agreement between Eqs. 10 and 11 and the experimental  $\chi$  data are similar, as can be seen from the  $R^2$  metrics in Table 1.

	Eq. 10		Eq. 11	
$c$ (M)	$\chi_0$	$K$	$\chi_0'$	$K'$
$[c_S \text{ range}]$				
0.05	$0.486 \pm 0.009$	$0.016 \pm 0.003$	$0.52 \pm 0.01$	$0.041 \pm 0.007$
$[3 - 0.15 \text{ M}]$	$R^2 = 0.97$		$R^2 = 0.98$	
0.1	$0.50 \pm 0.01$	$0.019 \pm 0.007$	$0.52 \pm 0.01$	$0.046 \pm 0.012$
$[3 - 0.3 \text{ M}]$	$R^2 = 0.91$		$R^2 = 0.95$	
0.2	$0.51 \pm 0.01$	$0.032 \pm 0.02$	$0.54 \pm 0.01$	$0.057 \pm 0.016$
$[3 - 0.75 \text{ M}]$	$R^2 = 0.97$		$R^2 = 0.99$	

TABLE 1: Best-fit values and 95% confidence intervals for  $\chi$  vs.  $c_S$  data fitted to  $\chi = \chi_0 - K/c_S$  and  $\chi = \chi_0' - K'/c_S^{1/2}$  at different polymer concentrations as indicated in the first column. The values in square brackets indicate the  $c_S$  range over which the preceding expressions were fitted. The  $R^2$  coefficient for each fit is indicated below the best-fit values.

An earlier estimate of  $\chi_0 \approx 1.1$  was obtained by Prabhu et al<sup>65,104</sup> by extrapolating  $\chi$  vs.  $1/c_S$  to infinite ionic strength for NaPSS in excess barium chloride. The larger value of  $\chi_0$  can be explained as arising from two factors: First, the NaPSS of reference 40 was synthesized by sulfonation of polystyrene, giving a degree of sulfonation of 96%, instead of 100% obtained for

samples made by radical polymerization of styrene sulfonate<sup>94</sup>, as is the case in the present work. The small fraction of non-sulfonated polystyrene is known to lead to greater backbone hydrophobicity, which manifests itself in, for example, smaller chain dimensions in dilute excess-salt solution and a lower  $\theta$ -salt concentration<sup>94,105</sup>. A second factor that may account for the discrepancy is that  $\text{Ba}^{2+}$  cations interact specifically with the sulfonate groups, leading to different chain conformations and phase behaviour<sup>65,104,106,107</sup>. It is possible that  $\chi$  exhibits a different  $c_s$  scaling in the presence of NaCl and  $\text{BaCl}_2$ , thus complicating a comparison of the extrapolations to infinite ionic strength.

The dependence of the  $\chi$  parameter on the square root of the added salt concentration is consistent with results reported for various polyelectrolyte systems<sup>66-70</sup>, and is also in line with Dobrynin et al's<sup>53</sup> and Odijk et al's<sup>108</sup> treatment of excluded volume in excess salt solutions, both of which expect the excluded volume strength to vary linearly with the Debye screening length.

## V. CONCLUSIONS

We have evaluated the correlation length and osmotic compressibility of polyelectrolyte solutions in excess salt. Scaling theory correctly describes the variation of the correlation length with the polymer concentration at low and moderate added salt concentrations, but at high salt concentrations the RPA and double screening theory work better. The ratio of the scattering correlation length and the osmotic correlation length is found to be  $\approx 4$  at high added salt concentration, in agreement with earlier reports for neutral polymers in good solvents. The correlation lengths obtained from the peak position in the scattering profiles of salt-free polyelectrolytes and from the fit to a Lorentzian function differ by an order of magnitude. The electrostatic  $\chi$  parameter is found to vary as  $\chi_{elec} \sim 1/c_s^{1/2}$ , in contrast with the linear dependence predicted by various theories. We quantified important similarities and differences between the behaviour of neutral polymers and polyelectrolytes in solutions at high salt concentrations. It is likely that at high salt concentrations the behavior of polyelectrolyte solutions is governed by hydrophobic interactions due to the hydrophobic nature of the backbone of the polyelectrolyte molecules.

## Acknowledgements

F.H and M.M. acknowledge the support of the Intramural Research Program of the NIH, NICHD. Access to the NGB 30m SANS was provided by the Center for High Resolution Neutron Scattering, a partnership between the National Institute of Standards and Technology and the National Science Foundation under Agreement No. DMR-1508249. Use of the NGB 10m SANS was supported by the NIST nSoft Consortium. We thank the ILL for beamtime. We thank Dr. B. Hammouda for his excellent advice.

## VI. REFERENCES

- <sup>1</sup>Bloomfield, V.A., *Biopolymers: Original Research on Biomolecules*, 1997, 44(3), pp.269-282.
- <sup>2</sup>D. Brandon and J. Tooze, *Introduction to Protein Structure*, Garland Publishing, London, New York, 1991
- <sup>3</sup>Klein, J., *Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology*, 2006, 220(8), pp.691-710.

- <sup>4</sup> Dédinaite, A., *Soft Matter*, 2012, 8(2), pp.273-284.
- <sup>5</sup> Meka, V.S., Sing, M.K., Pichika, M.R., Nali, S.R., Kolapalli, V.R. and Kesharwani, P., *Drug discovery today*, 2017, 22(11), pp.1697-1706.
- <sup>6</sup> Parhi, R., *Advanced pharmaceutical bulletin*, 2017, 7(4), pp.515-530.
- <sup>7</sup> Kayitmazer, A.B., Seeman, D., Minsky, B.B., Dubin, P.L. and Xu, Y., *Soft Matter*, 2013, 9(9), pp.2553-2583.
- <sup>8</sup> Moschakis, T. and Biliaderis, C.G., *Current opinion in colloid & interface science*, 2017, 28, pp.96-109.
- <sup>9</sup> Denton, A.R., Coarse-Grained Modeling of Charged Colloidal Suspensions: From Poisson-Boltzmann Theory to Effective Interactions. *Electrostatics of Soft and Disordered Matter*, p.201.
- <sup>10</sup> Wang, L., Lin, J. and Zhang, Q., *Soft Matter*, 2013, 9(15), pp.4015-4025.
- <sup>11</sup> Batys, P., Luukkonen, S. and Sammalkorpi, M., *Physical Chemistry Chemical Physics*, 2017, 19(36), pp.24583-24593.
- <sup>12</sup> Hsu, H.P. and Lee, E., *Electrochemistry Communications*, 2012, 15(1), pp.59-62.
- <sup>13</sup> Wypysek, S.K., Scotti, A., Alziyadi, M.O., Potemkin, I.I., Denton, A.R. and Richtering, W., *Macromolecular rapid communications*, 2020, 41(1), p.1900422.
- <sup>14</sup> Batys, P., Luukkonen, S. and Sammalkorpi, M., *Physical Chemistry Chemical Physics*, 2017, 19(36), pp.24583-24593.
- <sup>15</sup> Smiatek, J., *Molecules*, 2020, 25(7), p.1661.
- <sup>16</sup> Hansch, M., Hämisch, B., Schweins, R., Prévost, S. and Huber, K., *The Journal of chemical physics*, 2018, 148(1)
- <sup>17</sup> Kou, R., Zhang, J., Chen, Z. and Liu, G., *ChemPhysChem*, 2018, 19(11), pp.1404-1413.
- <sup>18</sup> Yu, J., Mao, J., Yuan, G., Satija, S., Jiang, Z., Chen, W. and Tirrell, M., *Macromolecules*, 2016, 49(15), pp.5609-5617.
- <sup>19</sup> Carl, N., Prévost, S., Schweins, R., Houston, J.E., Morfin, I. and Huber, K., *Macromolecules*, 2019, 52(22), pp.8759-8770.
- <sup>20</sup> Hansch, M., Kaub, H.P., Deck, S., Carl, N. and Huber, K., *The Journal of chemical physics*, 2018, 148(11), p.114906.
- <sup>21</sup> M. Rubinstein and R. H. Colby, *Polymer Physics* (Oxford, 2003).
- <sup>22</sup> P.-G. De Gennes and P.-G. Gennes, *Scaling concepts in polymer physics* (Cornell university press, 1979).
- <sup>23</sup> Bennett, A., Daivis, P.J., Shanks, R. and Knott, R., *Polymer*, 2004, 45(25), pp.8531-8540.
- <sup>24</sup> W. W. Graessley, *Polymeric liquids & networks: structure and properties* (Garland Science, 2003).
- <sup>25</sup> Huang, J.R. and Witten, T.A., *Macromolecules*, 2002, 35(27), pp.10225-10232.
- <sup>26</sup> Salamon, K., Aumiler, D., Pabst, G. and Vuletich, T., *Macromolecules*, 2013, 46(3), pp.1107-1118.
- <sup>27</sup> Horkay, F., Bassler, P.J., Hecht, A.M. and Geissler, E., *Macromolecules*, 2012, 45(6), pp.2882-2890.
- <sup>28</sup> Geissler, E., Hecht, A.M. and Horkay, F., 2010, May. Scaling Behavior of Hyaluronic Acid in Solution with Mono- and Divalent Ions. In *Macromolecular symposia* (Vol. 291, No. 1, pp. 362-370). Weinheim: WILEY-VCH Verlag.
- <sup>29</sup> Lopez, C.G. and Richtering, W., *The Journal of chemical physics*, 2018, 148(24), p.244902.

- <sup>30</sup> Tsuji, Y., Li, X. and Shibayama, M., *Gels*, 2018, 4(2), p.50.
- <sup>31</sup> Matsunaga, T., Sakai, T., Akagi, Y., Chung, U.I. and Shibayama, M., *Macromolecules*, 2009, 42(16), pp.6245-6252.
- <sup>32</sup> Shibayama, M., *Polymer journal*, 2011, 43(1), p.18.
- <sup>33</sup> Lopez, C.G., Colby, R.H. and Cabral, J.T., *Macromolecules*, 2018, 51(8), pp.3165-3175.
- <sup>34</sup> Yethiraj, A., *Physical review letters*, 1997, 78(19), p.3789.
- <sup>35</sup> von Solms, N. and Chiew, Y.C., *The Journal of chemical physics*, 2003, 118(9), pp.4321-4330.
- <sup>36</sup> Jiang, J.W., Blum, L., Bernard, O. and Prausnitz, J.M., *Molecular Physics*, 2001, 99(13), pp.1121-1128.
- <sup>37</sup> Jiang, J., Liu, H. and Hu, Y., *The Journal of chemical physics*, 1999, 110(10), pp.4952-4962.
- <sup>38</sup> Jiang, J., Liu, H., Hu, Y. and Prausnitz, J.M., *The Journal of chemical physics*, 1998, 108(2), pp.780-784.
- <sup>39</sup> Von Solms, N. and Chiew, Y.C., *The Journal of chemical physics*, 1999, 111(10), pp.4839-4850.
- <sup>40</sup> Yethiraj, A., *The Journal of Physical Chemistry B*, 2009, 113(6), pp.1539-1551.
- <sup>41</sup> Shew, C.Y., Do, C., Hong, K., Liu, Y., Porcar, L., Smith, G.S. and Chen, W.R., *The Journal of chemical physics*, 2012, 137(2), p.024907.
- <sup>42</sup> Landsgesell, J., Nová, L., Rud, O., Uhlík, F., Sean, D., Hebbeker, P., Holm, C. and Košovan, P., *Soft matter*, 2019, 15(6), pp.1155-1185.
- <sup>43</sup> Carrillo, J.M.Y. and Dobrynin, A.V., *The Journal of Physical Chemistry B*, 2010, 114(29), pp.9391-9399.
- <sup>44</sup> Mantha, S. and Yethiraj, A., *The Journal of Physical Chemistry B*, 2015, 119(34), pp.11010-11018.
- <sup>45</sup> Ramachandran, S., Katha, A.R., Kolake, S.M., Jung, B. and Han, S., *The Journal of Physical Chemistry B*, 2013, 117(44), pp.13906-13913.
- <sup>46</sup> Yao, G., Zhao, J., Ramiseti, S.B. and Wen, D., *Industrial & Engineering Chemistry Research*, 2018, 57(50), pp.17129-17141.
- <sup>47</sup> Chremos, A. and Douglas, J.F., *The Journal of chemical physics*, 2018, 149(16), p.163305.
- <sup>48</sup> Chremos, A. and Douglas, J.F., *The Journal of chemical physics*, 2017, 147(24), p.241103.
- <sup>49</sup> Soysa, W.C., Dünweg, B. and Prakash, J.R., *The Journal of chemical physics*, 2015, 143(6), p.064906.
- <sup>50</sup> Adamczyk, Z., Morga, M., Kosior, D. and Batys, P., *The Journal of Physical Chemistry C*, 2018, 122(40), pp.23180-23190.
- <sup>51</sup> Stevens, M.J. and Kremer, K., *The Journal of chemical physics*, 1995, 103(4), pp.1669-1690.
- <sup>52</sup> Carrillo, J.M.Y. and Dobrynin, A.V., *Macromolecules*, 2011, 44(14), pp.5798-5816.
- <sup>53</sup> Dobrynin, A.V., Colby, R.H. and Rubinstein, M., *Macromolecules*, 1995, 28(6), pp.1859-1871.
- <sup>54</sup> Carrillo, J.M.Y. and Dobrynin, A.V., *Polymers*, 2014, 6(7), pp.1897-1913.
- <sup>55</sup> Liao, Q., Dobrynin, A.V. and Rubinstein, M., *Macromolecules*, 2003, 36(9), pp.3399-3410.
- <sup>56</sup> Rubinstein, M., Colby, R.H., Dobrynin, A.V. and Joanny, J.F., *Macromolecules*, 1996, 29(1), pp.398-406.
- <sup>57</sup> – Ullner, M., Qamhieh, K. and Cabane, B., *Soft matter*, 2018, 14(28), pp.5832-5846.
- <sup>58</sup> Chang, R., Kim, Y. and Yethiraj, A., *Macromolecules*, 2015, 48(19), pp.7370-7377.
- <sup>59</sup> Lopez, C.G., *ACS Macro Letters*, 2019, 8(8), pp.979-983.

- <sup>60</sup> Xu, G., Luo, S., Yang, Q., Yang, J. and Zhao, J., *The Journal of chemical physics*, 2016, *145*(14), p.144903.
- <sup>61</sup> Xu, G., Yang, J. and Zhao, J., *The Journal of chemical physics*, 2018, *149*(16), p.163329.
- <sup>62</sup> Spiteri, M.N., Boué, F., Lapp, A. and Cotton, J.P., *Physical review letters*, 1996, *77*(26), p.5218.
- <sup>63</sup> Spiteri, M.N., Boue, F., Lapp, A. and Cotton, J.P., *Physica B: condensed matter*, 1997, *234*, pp.303-305.
- <sup>64</sup> Dubois, E. and Boué, F., *Macromolecules*, 2001, *34*(11), pp.3684-3697.
- <sup>65</sup> Prabhu, V.M., Muthukumar, M., Wignall, G.D. and Melnichenko, Y.B., *Polymer*, 2001, *42*(21), pp.8935-8946.
- <sup>66</sup> Iwamoto, Y., Hirose, E. and Norisuye, T., *Polymer journal*, 2000, *32*(5), pp.428-434
- <sup>67</sup> Hayashi, K., Tsutsumi, K., Norisuye, T. and Teramoto, A., *Polymer journal*, 1996, *28*(10), pp.922-928.
- <sup>68</sup> Yashiro, J., Hagino, R., Sato, S. and Norisuye, T., *Polymer journal*, 2006, *38*(1), pp.57-63.
- <sup>69</sup> Yashiro, J. and Norisuye, T., *Journal of Polymer Science Part B: Polymer Physics*, 2002, *40*(23), pp.2728-2735.
- <sup>70</sup> Tsutsumi, K. and Norisuye, T., *Polymer journal*, 1998, *30*(4), pp.345-349.
- <sup>71</sup> Brown, W. and Nicolai, T., *Colloid and polymer science*, 1990, *268*(11), pp.977-990.
- <sup>72</sup> Broseta, D., Leibler, L., Lapp, A. and Strazielle, C., *EPL (Europhysics Letters)*, 1986, *2*(9), p.733.
- <sup>73</sup> Shibayama, M., Tanaka, T. and Han, C.C., *The Journal of chemical physics*, 1992, *97*(9), pp.6829-6841.
- <sup>74</sup> Horkay, F., Han, M.H., Han, I.S., Bang, I.S. and Magda, J.J., *Polymer*, 2006, *47*(21), pp.7335-7338.
- <sup>75</sup> Lopez, C.G., Lohmeier, T., Wong, J.E. and Richtering, W., *Journal of colloid and interface science*, 2019, *558*, pp.200-210.
- <sup>76</sup> For NaPSS in aqueous solution,  $f \approx 0.2-0.3$ , see refs. 52-56 and this condition is therefore satisfied when  $c\zeta \gg c/20$ , which is met for all solutions considered in this work except those in salt-free D<sub>2</sub>O.
- <sup>77</sup> Colby, R.H., Boris, D.C., Krause, W.E. and Tan, J.S., *Journal of Polymer Science Part B: Polymer Physics*, 1997, *35*(17), pp.2951-2960.
- <sup>78</sup> Bordi, F., Cametti, C. and Colby, R.H., *Journal of Physics: Condensed Matter*, 2004, *16*(49), p.R1423.
- <sup>79</sup> Böhme, U. and Scheler, U., *Macromolecular Chemistry and Physics*, 2007, *208*(19-20), pp.2254-2257.
- <sup>80</sup> Huber, K. and Scheler, U., *Current opinion in colloid & interface science*, 2012, *17*(2), pp.64-73.
- <sup>81</sup> Destrée, M., Lyulin, A. and Ryckaert, J.P., *Macromolecules*, 1996, *29*(5), pp.1721-1727.
- <sup>82</sup> Müller, M., Binder, K. and Schäfer, L., *Macromolecules*, 2000, *33*(12), pp.4568-4580.
- <sup>83</sup> Cotton, J.P., Nierlich, M., Boue, F., Daoud, M., Farnoux, B., Jannink, G., Duplessix, R. and Picot, C., *The Journal of Chemical Physics*, 1976, *65*(3), pp.1101-1108.

- 84 Hamada, F., Kinugasa, S., Hayashi, H. and Nakajima, A., *Macromolecules*, 1985, 18(11), pp.2290-2294.
- 85 Stepanek, P., Perzynski, R., Delsanti, M. and Adam, M., *Macromolecules*, 1984, 17(11), pp.2340-2343.
- 86 Colby, R.H., *Rheologica Acta*, 2010, 49(5), pp.425-442.
- 87 Flory, P.J. and Daoust, H., *Journal of Polymer Science*, 1957, 25(111), pp.429-440.
- 88 Graessley, W.W., *Macromolecules*, 2002, 35(8), pp.3184-3188.
- 89 Vilgis, T.A. and Borsali, R., *Physical Review A*, 1991, 43(12), p.6857.
- 90 Vilgis and Borsali's theory is, as discussed in their paper valid only for strongly charged polyelectrolytes when their conformation can be assumed to be Gaussian at long distance scales (more specifically, when electrostatic stiffening does not cause a strong deviation of  $P(q)$  from that of the Debye form factor at low  $q$ ). For the high concentrations of added salt considered in this experiment, we expect this condition to be met.
- 91 Muthukumar, M., *The Journal of chemical physics*, 1996, 105(12), pp.5183-5199.
- 92 Certain Commercial Equipment, Instruments, or Materials Are Identified in This Paper in Order to Specify the Experimental Procedure Accurately. Such Identification Is Not Intended to Imply Recommendation or Endorsement by the National Institute of Standards and Technology, nor Is It Intended to Imply That the Materials or Equipment Identified Are Necessarily the Best Available for the Purpose.
- 93 Kassapidou, K., Jesse, W., Kuil, M.E., Lapp, A., Egelhaaf, S. and Van der Maarel, J.R.C., *Macromolecules*, 1997, 30(9), pp.2671-2684.
- 94 Hirose, E., Iwamoto, Y. and Norisuye, T., *Macromolecules*, 1999, 32(25), pp.8629-8634.
- 95 Hammouda, B. and Ho, D.L., *Journal of Polymer Science Part B: Polymer Physics*, 2007, 45(16), pp.2196-2200
- 96 Hammouda, B., Ho, D. and Kline, S., *Macromolecules*, 2002, 35(22), pp.8578-8585.
- 97 Nicolai, T. and Brown, W., *Macromolecules*, 1990, 23(12), pp.3150-3155.
- 98 Horkay, F., Tasaki, I. and Basser, P.J., *Biomacromolecules*, 2000, 1(1), pp.84-90.
- 99 Nierlich, M., Williams, C.E., Boue, F., Cotton, J.P., Daoud, M., Famoux, B., Jannink, G., Picot, C., Moan, M., Wolff, C. and Rinaudo, M., *Journal de Physique*, 1979, 40(7), pp.701-704.
- 100 Kaji, K., Urakawa, H., Kanaya, T. and Kitamaru, R., *Journal de Physique*, 1988, 49(6), pp.993-1000.
- 101 In salt-free solution, the correlation length is calculated as  $\xi_{SF} = 2\pi/q^*$ , where  $q^*$  is the scattering wave-vector of the peak in the scattering intensity.
- 102 M. Spiteri, "Thesis, Universite Orsay – Paris-Sud, 1997.
- 103 Norisuye and co-workers report data in the 0.05-4.17 M  $c_S$  range. The values quoted are interpolated for  $c_S = 3M$ .
- 104 Prabhu, V.M., Muthukumar, M., Wignall, G.D. and Melnichenko, Y.B., *The Journal of chemical physics*, 2003, 119(7), pp.4085-4098.
- 105 Takahashi, A., Kato, T. and Nagasawa, M., *The Journal of Physical Chemistry*, 1967, 71(7), pp.2001-2010.

<sup>106</sup> Požar, J., Bohinc, K., Vlachy, V. and Kovačević, D., *Physical Chemistry Chemical Physics*, 2011, *13*(34), pp.15610-15618.

<sup>107</sup> Zhang, Y., Douglas, J.F., Ermi, B.D. and Amis, E.J., *The Journal of Chemical Physics*, 2001, *114*(7), pp.3299-3313.

<sup>108</sup> Odijk, T. and Houwaart, A.C., *Journal of Polymer Science: Polymer Physics Edition*, 1978, *16*(4), pp.627-639.

SANS measurements on NaPSS solutions in excess NaCl show systematic deviations from the scaling theory and the random phase approximation.

