Polyelectrolytes in dilute solution: viscometric access to coil dimensions and salt effects

Journal:	*RSC Advances*
Manuscript ID:	RA-ART-01-2015-001376.R1
Article Type:	Paper
Date Submitted by the Author:	09-Mar-2015
Complete List of Authors:	Wolf, Bernhard; Institut für Physikalische Chemie, Johannes-Gutenberg Universität, Jakob-Welder-Weg 13, D-55099 Mainz, Germany, Badiger, Manohar; National Chemical Laboratory, Polymer Science and Engineering Suresha, P; National Chemical Laboratory, Polymer Science and Engineering

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Polyelectrolytes in dilute solution: viscometric access to coil dimensions and salt effects

P. R. Suresha [a], Manohar V. Badiger* [a,b] and Bernhard A. Wolf [b]*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Copolymers of acrylamide (AM) and diallyldimethylammonium chloride (DADMAC), differing in molar masses M (52.3 to 227 kDa) and degrees of charging y (0.2 to 0.6), were studied with respect to their viscometric behavior in dilute aqueous solutions containing variable amounts of NaCl. Complementary measurements were performed on a Brookhaven 90 plus particle size analyzer. M dominates the intrinsic viscosities $[\eta]$. For the viscometric interaction parameters B this is only true for large concentrations of extra salt. $[\eta]$ and B as a function of solvent salinity follow Boltzmann laws. Coil dimensions, determined either via dynamic light scattering or viscometry, agree well. For low salt contents of the solvent the radii decrease with rising polymer concentration, whereas they increase for high salt concentrations; at a characteristic salinity of the solvent they become independent. Zeta potentials grow from + 20 to + 40 mV as y goes up.

Introduction

Intrinsic viscosities, $[\eta]$, are conventionally obtained from so-called Huggins plots[1] as the y-intercept of the dependence of the reduced viscosity on polymer concentration (mass per unit volume). This procedure works well with uncharged macromolecules. However, in the case of polyelectrolytes, the electrostatic repulsion between the charged groups leads to a non-linear variation of the reduced viscosity with polymer concentration in the highly dilute regime hindering the reliable determination of $[\eta]$. For that reason we have developed an alternative approach[2] using the tools of phenomenological thermodynamics and enabling an unequivocal measurement of intrinsic viscosities for charged polymers. Under the presumption that the viscosity constitutes a variable state, $[\eta]$ is given by the initial slope of the dependence of the natural logarithm of the relative viscosity, ln η_{rel} (η_{rel}= viscosity of solution/viscosity of solvent) on polymer concentration. This method, also working for uncharged and non-linear macromolecules, is being increasingly used. [3-6]

In the present communication, we apply the above mentioned alternative approach to a further class of polyelectrolytes, namely to cationic copolymers of acrylamide (AM) and diallyldimethylammonium chloride (DADMAC), varying the content of DADMAC, i.e. changing their degree of charging. Particular attention is being paid to the possibility of obtaining dimensions of individual polyelectrolyte coils in solution from viscometric measurements. Information on the physicochemical behavior of the present polycations in dilute aqueous solution is not only of interest for basic research but also for industrial applications. In recent years poly(AM-*ran*-DADMAC) has become of special importance as retention aids in paper making[7], as flocculants in waste water treatment, mineral recovery and various other industrial separation processes.[8-10]

Polymer synthesis

The monomer DADMAC undergoes cyclopolymerization and yields in combination with AM poly(AM-*ran*-DADMAC), of the structure shown in **Figure 1**.

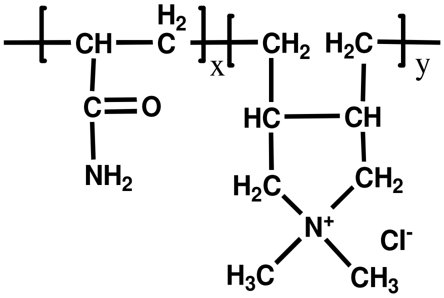


Figure 1: *y* is the mol fraction of DADMAC and *x* is that of AM

Acrylamide (AM) was purchased from Fluka, USA and was used as such; diallyldimethylammonium chloride (DADMAC) (65 wt-% solution in water) was purchased from Aldrich, USA; ammonium persulphate, sodium metabisulphite and sodium chloride were purchased from SD-fine chemicals, Mumbai, India which were of analytical grade and used as received. Sodium nitrate was purchased from Merck (India) and used as received. Deionized water (conductivity 0.055 µS/cm at 25°C) was used in all reactions and distilled acetone was used for precipitation of the polymer.

Copolymers of acrylamide with DADMAC were synthesized by solution polymerization using ammonium persulphate and sodium metabisulphite as redox initiator system. In a typical experiment, the calculated amounts of acrylamide and DADMAC solution (65%) were added to a 100 ml DI water in a double jacketed reaction vessel equipped with circulating water bath to maintain the desired reaction temperature. The stirring of the reaction mass was facilitated using a magnetic stirrer with the bar. The acrylamide concentration in the reaction mixture was maintained at 10 wt-% and the DADMAC contents were varied. The reaction mixture was purged with nitrogen for 30 min and temperature was increased to 40° C. Then ammonium persulphate and sodium metabisulphite were added to obtain an initiator concentration of 2 mol% and stirring continued. The reaction mixture became viscous and the polymerization was further carried out for 6 hrs. Finally, the polymer was precipitated in acetone and dried in vacuum oven at 40° C. Copolymers with different contents of DADMAC were synthesized. The mol fractions of DADMAC in the copolymers were obtained by NMR spectroscopy. The ^{1}H NMR spectrum of the copolymer shows the AM peak at 2.3 ppm and that of DADAMAC at 2.78 ppm. The area under the peak for single protons of AM and DADMAC was calculated, it yields the moles of AM and DADMAC. Taking the molecular weights of AM (71.08 g/mol) and DADMAC (161.67 g/mol) into consideration, the mol fraction of the DADMAC is 0.12, 0.32 and 0.44 for feed ratios of 80:20; 50:50 and 40:60; **Table 1** collects the data. Due to the unfavorable copolymerization kinetics the possibilities to vary the molar mass and the composition of the synthesized product independently are limited.

Table 1: Compositions, molar masses and polydispersity of the copolymers

y mol fraction DADMAC	M_w/kDa GPC	PDI
0.12	227.0	2.6
0.32	93.4	2.2
0.44	52.3	1.5

Figure 2 compares the 1H NMR spectrum of poly(AM-*ran*-DADMAC) with that of polyacrylamide. It can be readily seen that the peaks of DADMAC appear in the range of 2.7-4.0 ppm. This confirms the incorporation of DADMAC into the copolymer.

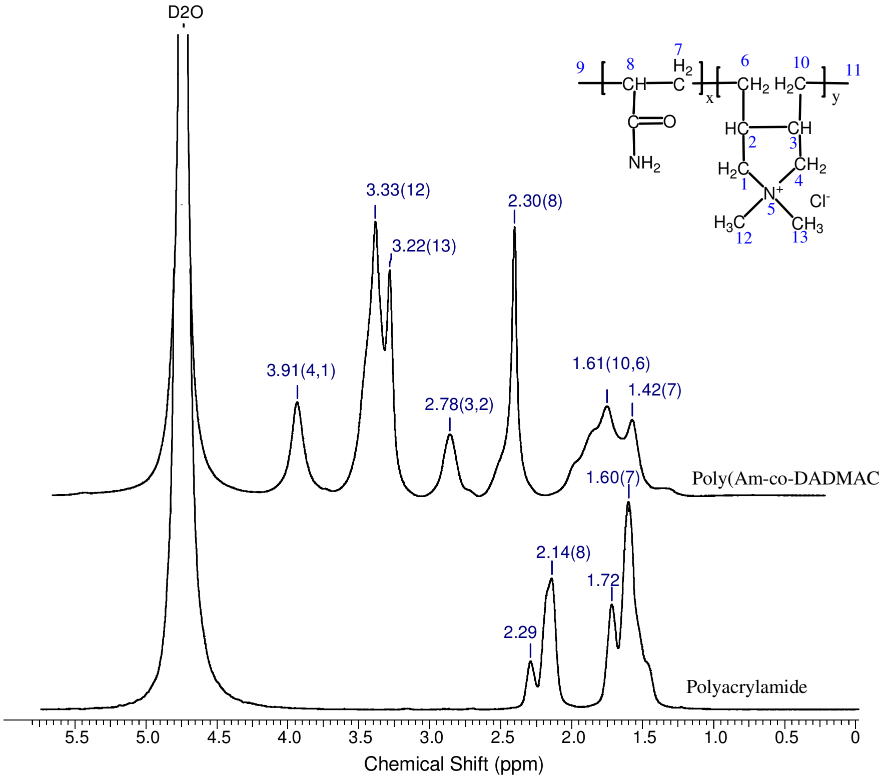


Figure 2: ^{1}HNMR spectra of the copolymer and of PAM

Experimental procedures

Gel Permeation Chromatography Samples were analyzed using Agilent 1200 series GPC system with Shodex OHpak SB 800 series columns. The mobile phase was 0.25 N $NaNO_3$ and pumped at 0.4 mL/min with injection volume 200 µL and the column temperature was 40°C. Polyacrylamide standards were used for calibration.

Viscosity measurements Viscosity measurements were performed using a Ubbelohde capillary viscometer with capillary diameter 0.63 mm in combination with AVS 470 (SCHOTT Geräte, Mainz, Germany). The measurements were carried out either in pure deionized water or in NaCl solutions (0.0003 to 1 M). Measurements were performed at 25°C ±0.05° C. For pure deionized water the polymer concentrations varied from 0.01 to 0.05 g/dL but for NaCl solutions the concentration was in the range of 0.1 to 0.5 g/dL due to the decrease in the viscosity of the solutions.

Zeta potential measurement Zeta potential measurements were done at 25 °C using Brookhaven 90 plus particle size analyzer instrument. The polymer concentration was 0.1 g/dL in deionized water.

Hydrodynamic radii Hydro dynamic radii (Rh) were measured using Brookhaven 90 plus particle size analyzer. The experiments were performed at 90° monitoring the variation in the intensity of the scattered light caused by the Brownian motion of the particles. The polymer solutions of known concentrations in deionized water were filtered through 0.22 µ filters (Millipore syringe filter).

Data evaluation

Intrinsic viscosities of polyelectrolytes in aqueous solutions containing no extra salt cannot be determined by the traditional means (for instance using the Huggins[1] equation). For that reason we employ a different method based on the description of η as a complete differential[2]. As long as the viscosity η represents a variable of state, this approach is applicable to virtually all kinds of macromolecules. It introduces a generalized intrinsic viscosity for arbitrary polymer concentrations c (mass per volume)

$$\{\eta\} = \left(\frac{\partial \ln \eta}{\partial c}\right)_{T,p,\dot{\gamma}} \qquad (1)$$

as the slope of concentration dependence of the natural logarithm of η at constant values of temperature, pressure and shear rate. For Newtonian behavior and in the limit of infinite dilution $\{\eta\}$ becomes identical with the intrinsic viscosity.

$$\lim_{\substack{c \to 0 \\ \dot{\gamma} \to 0}} \{\eta\} = [\eta] \tag{2}$$

The results of the capillary measurement were evaluated in terms of relative viscosities η_{rel} by means of the following relation[2]

$$\ln \eta_{rel} = \frac{c[\eta] + Bc^2[\eta][\eta]^{\bullet}}{1 + Bc[\eta]} \tag{3}$$

B represents a viscometric interaction parameter (by analogy to the well-known Huggins coefficient). In the case of polyelectrolytes it can be subdivided into B_{coul} (electrostatic contribution) and $B_{\mathrm{n\text{-}coul}}$ (residual interaction)

$$B = B_{coul} + B_{n-coul} \tag{4}$$

The additional parameter $[\eta]^{\bullet}$ is required to model the observation that ln η_{rel} as a function of c becomes linear within experimental error at sufficiently high concentrations. The applicability of equation (3) is not confined to polyelectrolytes; for solutions of uncharged macromolecules $[\eta]^{\bullet} = 0$ and two parameters suffice for their modeling.

The generalized intrinsic viscosity (equation (1)) can be calculated from the measured concentration dependence of the relative viscosity (equation (3)). Writing $\tilde{c}$ for the reduce polymer concentration (similar to but not identical with the coil overlap parameter) and r for the ratio of the intrinsic viscosity and the parameter $[\eta]^{\bullet}$

$$\tilde{c} = c[\eta] \text{ and } \qquad r = \frac{[\eta]^{\bullet}}{[\eta]} \tag{5}$$

one obtains the following expression

$$\{\eta\} = [\eta] \frac{1 + 2Br\tilde{c} + B^2 r\tilde{c}^2}{1 + 2B\tilde{c} + B^2\tilde{c}^2} \tag{6}$$

For the modeling of the influences of the solvent salinity on the parameters of equation (3) the following Boltzmann relations turned out to be suited best according to earlier experiments[11]

$$\log[\eta] = \log[\eta]_{\mathrm{o}} + \frac{\log[\eta]_{\infty} - \log[\eta]_{\mathrm{o}}}{1 + \exp\left(H \log\left(c_{\mathrm{salt}} / c_{\mathrm{salt}}^{\mathrm{pi}}\right)\right)} \tag{7}$$

for the intrinsic viscosities $[\eta]$ and

$$B = B_{\mathrm{o}} + \frac{B_{\infty} - B_{\mathrm{o}}}{1 + \exp\left(H \log\left(c_{\mathrm{salt}} / c_{\mathrm{salt}}^{\mathrm{pi}}\right)\right)} \tag{8}$$

for the viscometric interaction parameter B. The index zero signifies the values of the parameters in the absence of salt and the index infinity the limiting value at high salt concentrations; $c_{\mathrm{salt}}^{\mathrm{pi}}$ stands for the salt concentration at the point of inflection and H is a parameter quantifying the steepness of the transitions.

For the comparison of R_{DLS}, the radius of the polymer coils resulting from dynamic light scattering, with the radius $R_{\{\eta\}}$ obtained from the viscometric behavior we make use of the following relation[12]

$$R_{[\eta]}^{3} = \frac{[\eta] M_w}{6^{3/2} \Phi_o} \tag{9}$$

where we set the constant $\Phi_o = 2.5\ 10^{23}$ according to literature.[13] Under the reasonable assumption that the above relation remains applicable if the intrinsic viscosity is replaced by the general intrinsic viscosity $\{\eta\}$ we can write

$$R_{\{\eta\}}^{3} = \frac{\{\eta\} M_w}{6^{3/2} \Phi_o} \tag{10}$$

and gain access to the dependence of coil dimensions on polymer concentration.

In order to obtain information on the average salt concentration inside an isolated coil in the absence of extra salt (exclusively caused by the charged units of the polyelectrolyte), we calculate its molar volume by means of $[\eta]_o$, the intrinsic viscosity in the absence of extra salt, and equation (9) according to

$$V_{\text{isolated polymer coil}} = \Gamma [\eta]_o M_w \tag{11}$$

where the parameter $\Gamma = 4\,\pi N_L / (3{*}6^{3/2}\,\Phi_o) = 0.687$ collects all numerical factors; N_L is the Avogadro number. Denoting the number of charges per charged monomer unit by z (here equal to unity) and the total number of monomeric units of the copolymer by N, the number of charges per macromolecules is equal to $z\,y\,N$, where y is the mol fraction of charged DADMAC units again. The salt concentration, $c_{salt}^{()}$, inside an isolated coil thus becomes

$$c_{salt}^{()} = \frac{z\,y\,N}{\Gamma [\eta]_o M} \tag{12}$$

Results and Discussion

This part is organized in the following manner: The first section deals with the viscometric behavior of dilute solutions of the different polyelectrolytes in pure, deionized water. The second and main part is dedicated to the effects of extra salt on intrinsic viscosities and viscometric interaction parameters. The third paragraph addresses the concentration dependence of the dimensions of the polyelectrolyte coils and reports zeta potentials for different cationic polyelectrolytes.

The ranges of polymer concentrations investigated for the different samples account for their pronouncedly dissimilar molar masses. In case of y=0.12 (227 kDa) the maximum c was 0.05 g/dL; for the lower molecular weight samples y=0.32 and 0.44 it was 0.5 g/dL. The corresponding maximum reduced polymer concentrations $\tilde{c}_{max}$ are (in the above order of y) for pure water 1.33, 5.63 and 3.37; for high salinity of the solvent they are 0.08, 0.22 and 0.12.

Viscometric behavior in pure water

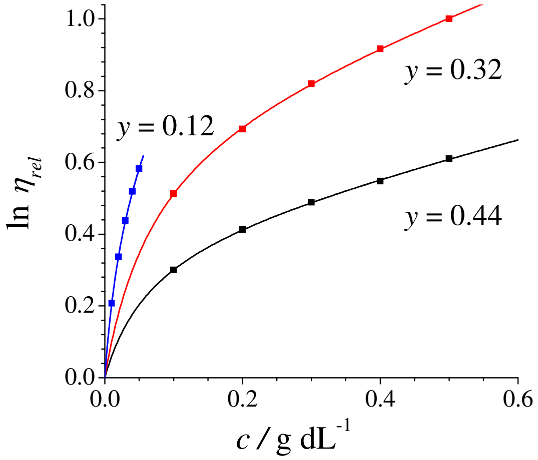


Figure 3: Concentration dependence of the viscosity for aqueous solutions of the copolymers in the absence of extra salt. The mol fractions of DADMAC, y, are indicated in the graph.

The characteristic parameters obtained from the dependencies shown in **Figure 3** are collected in **Table 2**. The sample with the highest molar mass and the lowest degree of substitution exhibits the largest $[\eta]$ value and the sample with the largest y and lowest M shows the least $[\eta]$, i.e. y and M act in the opposite direction. The present finding suggests a predominance of the effects of chain lengths over that of the fraction of charged units, at least in the range of present measurements.

The hydrodynamic interaction parameter B (quantifying the deviation of ln η_{rel} vers. c from the linear dependence) is in the present case (absence of extra salt) always positive. This means that the viscosity of the solution increases less than exponentially upon the augmentation of the polymer concentration for all samples. This behavior is typical for thermodynamically good solvents. In the case of sufficiently unfavorable solvents the viscosity rises more than exponentially with c and B becomes negative (cf. **Figure 8**). The influences of molar mass agree qualitatively with that observed[14] for the system water/poly(styrene sulfonate). For aqueous solutions of cationic dextran derivatives the parameter B passes a pronounced maximum at low y values on the order of 0.15; for higher y values B declines steadily.[15, 16] The present results agree well with that behavior. Still to discuss is the parameter $[\eta]^{\bullet}$ (cf. equation (3)); its logarithm declines linearly with increasing log M like the dependence of B. This behavior is in accord with that reported for poly(styrene sulfonic acid).[14]

Table 2: Concentration dependence of the viscosity
of the copolymer solutions in pure water: Parameters of equation (3)

y	M_w/kDa	$[\eta]_o$ / mL/g	±	$[\eta]^{\bullet}$ / mL/g	±	B_o	±
0.12	227.0	2662	101	307	96.0	0.70	0.04
0.32	93.4	1126	47	66	3.8	1.22	0.04
0.44	52.3	674	38	47	2.8	2.18	0.10

We are now turning to the question how the generalized intrinsic viscosity $\{\eta\}$ in pure water depends on the polyelectrolyte concentration c. In other words we want to know how the hydrodynamic specific volume of the polyelectrolyte changes for the samples differing in molar mass and degree of charging. To that end we plot in **Figure 4** the relative change $\{\eta\}/[\eta]$ as a function of the reduced polymer concentration $c\,[\eta]$ for the samples of interest. The results demonstrate beyond doubt that it is the degree of charging y that governs the relative reduction in $\{\eta\}$ and that the molar mass M is of minor importance only. The physical reason for the drastic diminution of $\{\eta\}$ with rising polymer concentration lies in the electrostatic shielding of the repulsion between the charges of an individual polyelectrolyte molecule caused by the addition of further macromolecules.

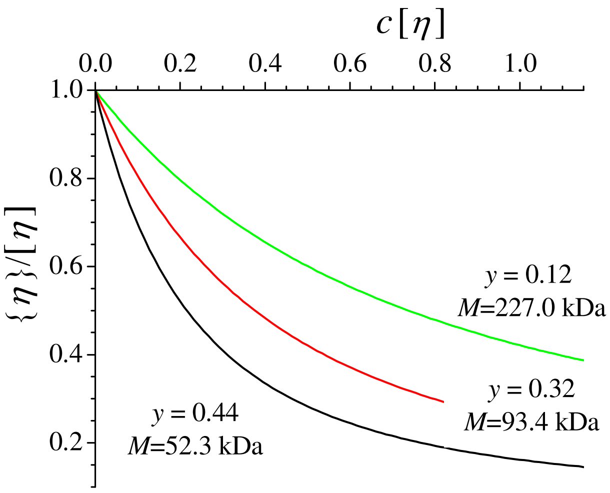
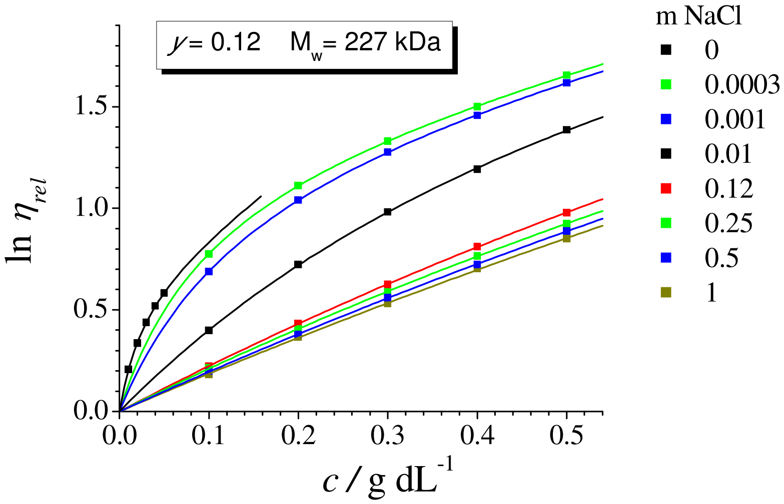


Figure 4: Coil shrinkage in the absence of extra salt upon an increase in polymer concentration.

5 **Effects of extra salt**

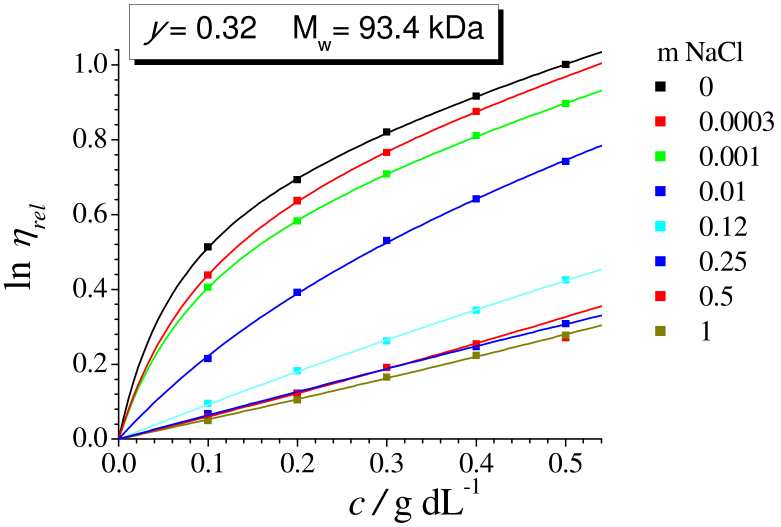
The following three graphs show how the viscosity increase caused by an increasing polyelectrolyte concentration is progressively suppressed as the salinity of the solvent rises.

Part a



10

Part b



Part c

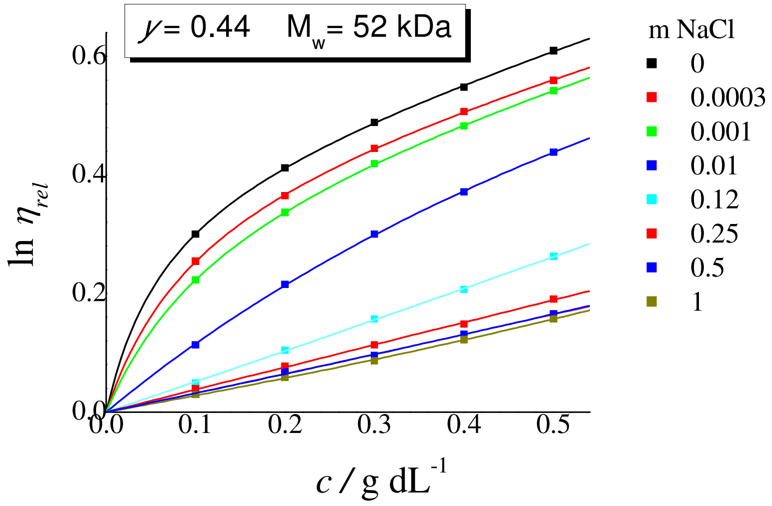


Figure 5: Relative viscosity as a function of polyelectrolyte concentration
for different solvent salinities.
Part a: y = 0.12 and M_{w} = 227 kDa,
part b: y = 0.32 and M_{w} = 93.4 kDa,
part c: y = 0.44 and M_{w} = 52 kDa

The evaluation of the primary data shown in **Figure 5** according to equation (3) yields the dependencies of $[\eta]$ and B on the salt concentration of the solvent (cf. **Table 3**). An analogous discussion of the effects for the parameter $[\eta]^{\bullet}$ is not worthwhile because it plays a minor role only, even for pure water, and dies out rapidly with increasing salt concentration. A comparison of the experimental observations with theoretical predictions[17-20] turns out to be difficult. Only the forecasts of the scaling theory[18] concerning the concentration dependence in the semidilute regime are testable. The predictions are not corroborated; the dependencies prove to be considerably more complicated.

Figure 6 describes the variation of the intrinsic viscosities in terms of Boltzmann dependencies (cf. equation (7)).

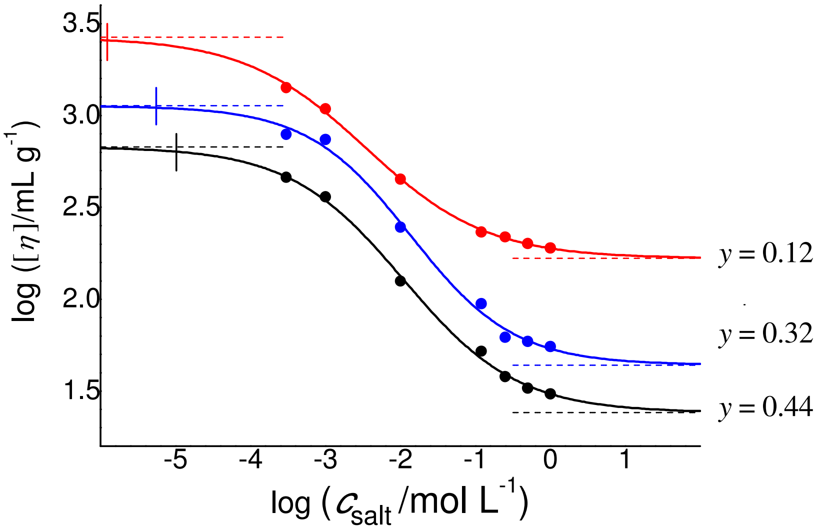


Figure 6: Dependence of the intrinsic viscosities of the indicated polyelectrolyte on the salt content of the solvent; the vertical lines designate the calculated salt concentration inside the isolated polyelectrolyte coils in the absence of extra salt, $c_{salt}^{()}$. The broken horizontal lines show the asymptotic behaviors in pure water and in the limit of high salt concentrations, respectively. The curves are drawn according to equation (7) using the parameters of Table 3.

For the present considerations we need to discuss two extreme cases for the state of individual polymer coils: (i) Their largest size in pure water and (ii) their least size in sufficiently saline solution. The probability for the joint occurrence of both states as a function of the salinity of the solvent can be described by a Boltzmann function. The integral of this Boltzmann function yields the cumulative distribution function, also called Boltzmann sigmoid. Its point of inflection divides the concentration range of extra salt into two domains: At lower salinity the majority of the polyelectrolyte molecules are in state (i), whereas they are predominantly in state (ii) at higher salinity.

Figure 6 evinces that the intrinsic viscosities start to decrease noteworthy upon an augmentation of the solvent salinity once the salt concentration surpasses $c_{salt}^{()}$, the salt concentration in an isolated coil for pure water. The changes in the $[\eta]$ values from $[\eta]_o$ (absence of extra salt) to $[\eta]_\infty$ (limiting value for a large surplus of extra salt) take place by and large in the range from 10^{-5} molar to 1 molar NaCl. In view of the fact that similar data were reported for solutions of polyanions[11, 14] and polycations of different chemistry[16, 21] in the case of monovalent salts, this result seems to be typical.

Figure 7 shows that log $([\eta]_\infty / [\eta]_o)$ as a function of the degree of charging exhibits a saturation behavior. The changes in the intrinsic viscosities are largest in the limit of vanishing y and level off for $y \to 1$. A comparison of the present results with earlier data for partly charged dextran copolymers[16] shows remarkable differences for large y values. For poly(AM-*ran*-DADMAC) the maximum reduction amounts to 1/30, whereas it is 1/80 for the cationic dextran. This dissimilarity can probably be attributed to the largely different geometries of the polymer backbones.

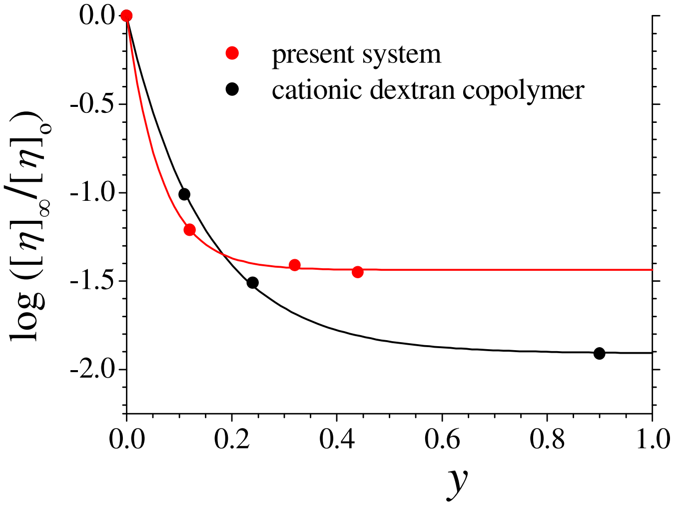


Figure 7: Maximum reduction of $[\eta]$ upon the addition of a large surplus of extra salt; the data for the cationic dextran copolymer are taken from the literature.[16]

So far we have dealt with the influences of salt on intrinsic viscosities, i.e. on isolated coils. We are now addressing salt effects on the viscometric interaction parameter B characterizing the pair interaction between the individual polyelectrolyte molecules. **Figure 8** shows these dependencies.

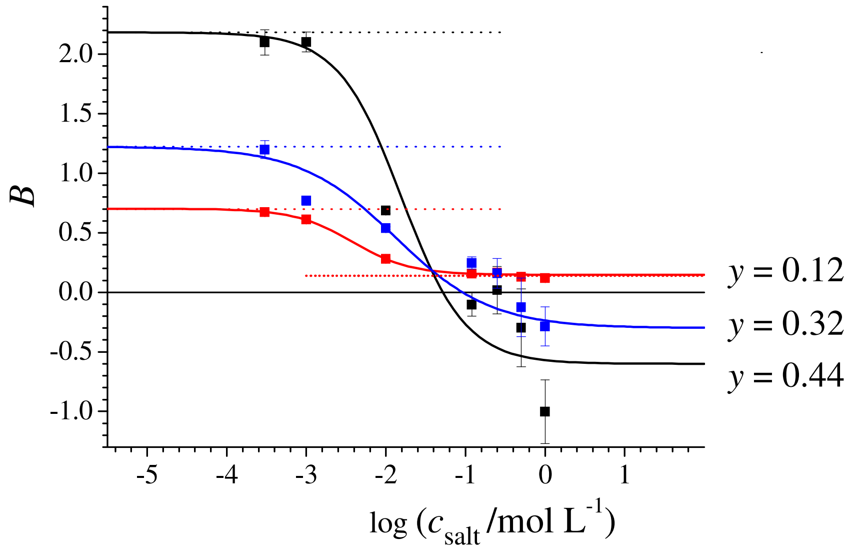


Figure 8: Dependence of the hydrodynamic interaction parameter B on the salinity of the solvent modeled according to equation (8). The pertinent parameters are given in **Table 3**

The most obvious difference in the salt influences on B as compared with that on $[\eta]$ is the intersection of the curves for different y values. The fact that all three curves do so at the same salt concentration is probably only fortuitous. The observed crossover of the curves can be explained in terms of the two parts B consists of (cf. equation (4)). In pure water B_{coul} dominates; this part is always positive because the polyelectrolyte coils shrink upon an increase in polymer concentration: The viscosity increase slows down (the curves ln η_{rel} vers. c are located below their tangents, corresponding to positive B values). B_{coul} is largest for the copolymer of highest charge density and explains the order of the curves at low salt concentrations.

The application of equation (4) for pure water (index zero) and for a large surplus of extra salt (index infinity) yields two relations. Under the reasonable assumptions that the non-Coulomb parts of B are the same in both cases and that the electrostatic interactions are completely shielded by enough salt ($B_{\text{coul},\infty} = 0$) we can write $B_o = B_{\text{coul, o}} + B_\infty$ and calculate $B_{\text{coul, o}}$, the Coulomb part of B in the case of pure water. Plotting the $B_{\text{coul, o}}$ values calculated by means of the data collected in **Table 3** as a function of y indicates a more than linear increase. The dependence starts at *y*=0 in agreement with the consideration that Coulomb interactions should be absent for the uncharged polymer. In the present case $B_{\mathrm{coul,\,o}}$ is 0.56, 1.52 and 2.87 in the order of increasing *y* values. Comparable results are calculated[21] from experiments published for sodium pectinate[22-24] ($B_{\mathrm{coul,\,o}}$ = 1.58 for y=1) and for cationic dextran derivatives[16] ($B_{\mathrm{coul,\,o}}$ = 2.4 for y=0.9). These dissimilarities indicate that the specific molecular and chemical structure of the polyelectrolyte modifies the Coulomb contribution to the viscometric interaction parameter *B*.

Figure 8 shows that the *B* values decrease with rising *y* at high salt concentrations; for *y* = 0.12 *B* is still positive but it becomes negative for the two samples of larger charge density. Less than zero interaction parameters express the fact that the viscosity of the solution rises more than exponentially upon an augmentation of polymer concentration. Because of the relation[14] k_H =0.5 – B, negative B values correspond to k_H values larger than 0.5, i.e. indicate poor thermodynamic qualities of the solvent. In order to verify this statement we have evaluated data published[25] for solutions of PMMA and PBMA in poor solvents by means of equation (3); the resulting *B* values are indeed on the order of – 0.35 to - 0.40. This result corroborates the above consideration. The pronounced worsening of solvent quality at large salt concentrations caused by the augmentation of *y* observed for the present system can tentatively be attributed to the chemical structure of the charged monomer (cf. **Figure 1**). Due to the large number of CH_2 - and CH_3 - groups the polyelectrolyte interacts unfavorably with water once the electrostatic interactions are sufficiently shielded by extra salt.

Table 3: Effects of the salinity of the solvent on the viscosities of the copolymer solutions as modeled by the parameters of equation (7) and (8), respectively; $c^{()}_{\mathrm{salt}}$ is the calculated (equation (12)) salt concentration inside an isolated coil in the absence of extra salt.

y	$[\eta]_o$ / mL/g	$[\eta]_\infty$ / mL/g	$\log c^{\mathrm{pi}}_{\mathrm{salt}}$ / mol/L	±	$\log c^{()}_{\mathrm{salt}}$ / mol/L	*H*	±
0.12	2662	166.7	-2.46	0.05	-5.91	1.24	0.06
0.32	1126	43.8	-1.87	0.13	-5.26	1.45	0.16
0.44	674	24.2	-1.96	0.09	-4.99	1.32	0.09
y	B_o	B_∞	$\log c^{\mathrm{pi}}_{\mathrm{salt}}$ / mol/L	±	$\log c^{()}_{\mathrm{salt}}$ / mol/L	*H*	±
0.12	0.70	0.14	-2.42	0.04	-5.91	2.59	0.19
0.32	1.22	-0.30	-1.88	0.06	-5.26	1.57	----
0.44	2.18	-0.60*	-1.80	----	-4.99	2.50	0.81

* Value read from **Figure 8**

Zeta potentials

Figure 9 displays the zeta potentials ζ as a function of y in the absence of extra salt measured for the present polymers and compares these findings with data reported in the literature[26] for linear cationic copolymers. All values are expectedly positive and increase with rising y. It would be interesting to compare these data with the zeta potentials of fully charged homopolymers, but surprisingly no such information could be found.

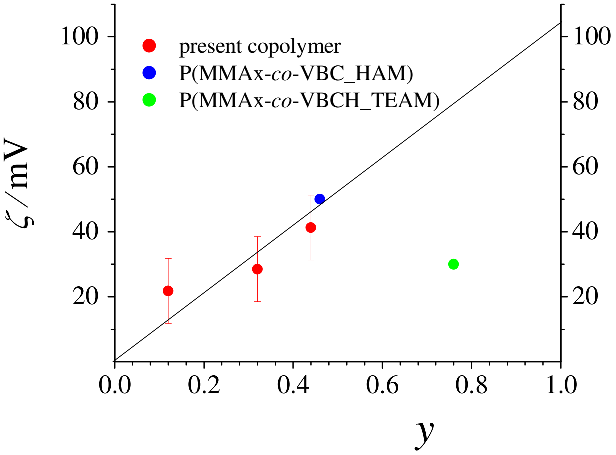


Figure 9: Zeta potentials for the present copolymers (polymer concentration 0.1 wt% and 25 °C) in aqueous solutions as a function of their degree of charging y and data reported for different cationic copolymers.[26]

The abbreviations P(MMAx-*co*-VBC_HAM) and P(MMAx-*co*-VBCH_TEAM) stand for copolymers which were synthesized from MMA plus VBC (4-vinylbenzyl chloride) and quaternized by means of HAM (N,N-dimethylhexadecylamine) or TEAM (triethylamine).

Hydrodynamic radii

Equation (9) gives access to the dimensions of polymer coils if the polymer mass and the generalized intrinsic viscosities are known, as formulated in the section dealing with the evaluation of viscometric data. In view of the fact that the intrinsic viscosities can be determined much easier than hydrodynamic radii by means of dynamic light scattering measurements, we are in the following comparing the radii obtained by means of the two methods. Figure 10 shows, as an example, the concentration dependence of coil dimensions for the least charged copolymer in water containing 0.25 mols NaCl per liter.

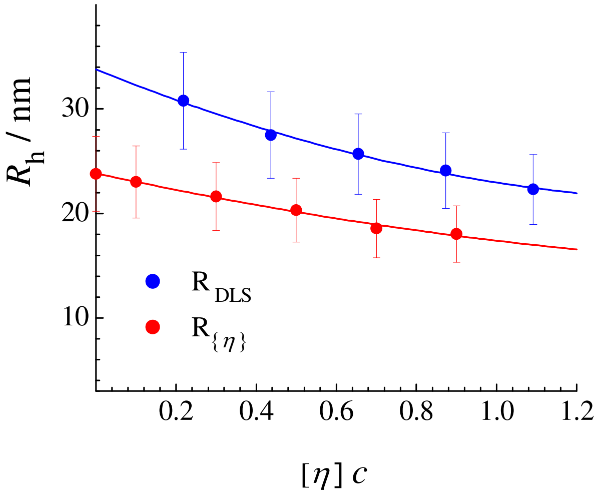


Figure 10: Comparison of the hydrodynamic radii of the polyelectrolyte coils as a function of the reduced polymer concentration obtained from DLS experiments and from viscometry (cf. equation (9)) for the copolymer sample of lowest charging (y=0.12) and water containing 0.25 mol NaCl per liter.

Both methods evince a diminution of coil dimensions upon an increase in polymer concentration. This observation is in accord with the still favorable thermodynamic conditions prevailing for low solvent salinity: The coils shrink as they approach the theta conditions that should be realized in the pure state of the hypothetical melt. The agreement between the numerical results of light scattering and viscometry looks worse than it is: The data obtained with the respective method scatter only moderately. Their systematic shift stems for the comparatively large polymolecularity of the sample and is in accord with the theoretical expectation.

The present finding testifies the equivalence of DLS and viscometric results. In view of this situation we have evaluated all viscosity data with respect to $R_{\{\eta\}}$. **Figure 11** gives an example for the copolymer of medium charging. It shows how the coil dimensions change with the reduced polymer concentration c $[\eta]$ for solvents differing in their salinity, including pure water, for which dynamic light scattering measurements would be problematic.

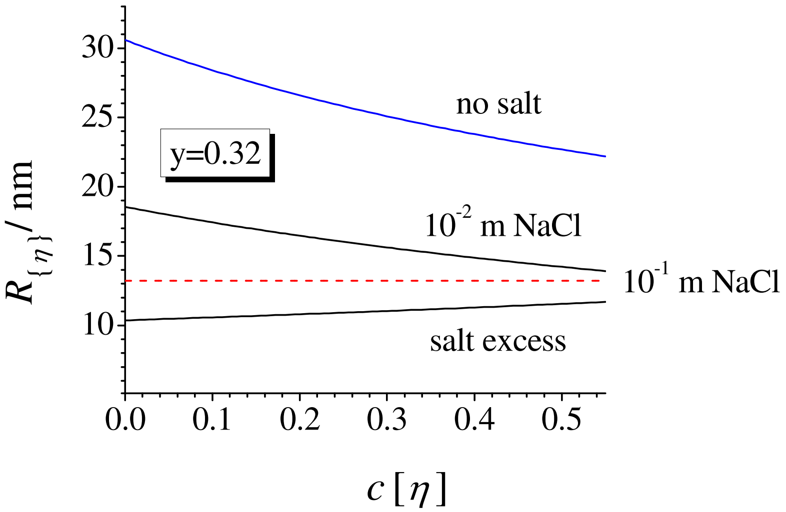


Figure 11: Coil dimensions calculated from the equations (10) and (6) by means of the parameters of **Table 3** as a function of the reduced polymer concentration for the polymer sample with the medium degree of charging (y=0.32). The salt contents of the solvents are indicated in the graph.

For low concentrations of external salt the coils shrink again as the polymer concentration rises because of the electrostatic shielding discussed above. The situation changes, however, for sufficiently high salt concentrations. Under these conditions the interaction of the charged units with water becomes considerably less favorable, as already manifested by the low $R_{[\eta]}$ value of the isolated molecules. In the case of sufficiently unfavorable solvents the coils expand as c $[\eta]$ increases and the number of more favorably interacting polymer segments rises. From these findings it is obvious that a characteristic salt concentration must exist at which the coil dimension become independent of polymer concentration. In the present case these conditions are realized as the solvent contains 0.1 mol/L NaCl.

Conclusions

For the present combination of M and y the intrinsic viscosities are under all conditions dominated by chain length. The reduction of $[\eta]_o$ and of B_o (the values of the intrinsic viscosity and of the hydrodynamic interaction parameter B in pure water) resulting from an increase in the concentration of extra salt are quantitatively described by Boltzmann relations. The deviations from this limiting behavior in pure water set in as soon as the salt concentration of solvent exceeds the average salt concentration inside an isolated coil in absence of extra salt. The curves for the intrinsic viscosities do not intersect. The maximum reduction of $[\eta]$ due to the salinity of the solvent as function of y shows an asymptotic behavior and varies from system to system. The dependencies of the hydrodynamic interaction parameter B as a function of salt concentration intersect. For solvents of little salinity the B values are all positive and the larger the higher the degree of charging. At large salt concentrations the opposite order is established and the values may become negative. This behavior can be rationalized by splitting B into a Coulombic and non-Coulombic part. The former contribution is always positive (as a result of the electrostatic shielding of the interactions caused by an increase in polymer concentration) in contrast to the latter contribution reflecting the intersegmental friction in the absence of charges; it may be either positive (less than exponential increase of the viscosity with rising polymer concentration) or negative (more than exponential increase).

Dynamic light scattering data and the generalized intrinsic viscosities give access to the dimensions of individual polyelectrolyte coils. In view of the good agreement between the two sets of data, the viscometric behavior was evaluated with respect to coil dimensions in detail. In the absence of external salt and at low salt concentrations the coils shrink expectedly upon an increase of polymer concentration. For a sufficiently high salinity of the solvent the opposite is the case; this behavior is due to the unfavorable thermodynamic quality of solvents containing much salt. This situation leads to an increase in the number of intersegmental contacts and to higher friction. At a certain characteristic salinity of the solvent, the dimensions become independent of polymer concentration.

The present investigation also provides information on zeta potentials. In agreement with theoretical expectation they are all positive for the polycations of interest and increase form + 20 to + 40 mV with rising *y*. These findings are in qualitative agreement with literature reports on partly charged polycations and polyanions. Surprisingly enough, no data on fully charged polyelectrolytes could be found in the literature.

Acknowledgements

MVB thanks the Alexander von Humboldt (AvH) Foundation Bonn, Germany for a revisit fellowship. The authors also acknowledge financial support from RGSTC Mumbai, India

Notes and references

[a] *Polymer Science and Engineering Division, National Chemical Laboratory (NCL), Pune- 411 008, India*
Fax: +91-20-2590 2612; Tel: +91-20-2590 2187; E-mail: mv.badiger@ncl.res.in

[b] *Institut für Physikalische Chemie, Jakob Welder-Weg 11, D-55099 Universität Mainz*
Tel: +49-6131-392 2491; E-mail: bernhard.wolf@uni-mainz.de

References

.

1 M. L. Huggins, *J. Am. Chem. Soc.*, 1942, **64**, 2716.

2 B. A. Wolf, *Macromol. Rapid Commun.*, 2007, **28**, 164.

3 A. Chatterjee and B. Das, *Carbohydr. Polym.*, 2013, **98**, 1297.

4 R. De and B. Das, *Polym. Int.*, 2014, **63**, 1959.

5 A. Spatareanu, M. Bercea, T. Budtova, V. Harabagiu, L. Sacarescu, S. Coseri and Epnoe, *Carbohydr. Polym.*, 2014, **111**, 63.

6 X. P. Xiong, Q. R. Ke and S. Q. Zhu, *Chin. J. Polym. Sci.*, 2014, **32**, 209.

7 E. Antunes, F. A. P. Garcia, P. Ferreira, A. Blanco, C. Negro and M. G. Rasteiro, *Industrial & Engineering Chemistry Research*, 2008, **47**, 9370.

8 M. A. Martin, I. Gonzalez, M. Berrios, J. A. Siles and A. Martin, *Chem. Eng. J.*, 2011, **172**, 771.

9 H. B. Li, Y. M. Du, X. J. Wu and H. Y. Zhan, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 2004, **242**, 1.

10 P. Somasundaran, K. K. Das and X. A. Yu, *Current Opinion in Colloid & Interface Science*, 1996, **1**, 530.

11 X. P. Xiong and B. A. Wolf, *Soft Matter*, 2014, **10**, 2124.

12 M. Martin Alberto and S. Maria Gabriela, *Hydrodynamic Properties of Gelatin - Studies from Intrinsic Viscosity Measurements*, INTECH Open Access Publisher, 2012.

13 A. Ortega and J. G. de la Torre, *Biomacromolecules*, 2007, **8**, 2464.

14 J. Eckelt, A. Knopf and B. A. Wolf, *Macromolecules*, 2008, **41**, 912.

15 L. Ghimici, M. Nichifor and B. Wolf, *J. Phys. Chem. B*, 2009, **113**, 8020.

16 L. Ghimici, M. Nichifor, A. Eich and B. A. Wolf, *Carbohydr. Polym.*, 2012, **87**, 405.

17 M. Sedlak, *Macromolecules*, 1995, **28**, 793.

18 A. V. Dobrynin, R. H. Colby and M. Rubinstein, *Macromolecules*, 1995, **28**, 1859.

19 P. Lorchat, I. Konko, J. Combet, J. Jestin, A. Johner, A. Laschewski, S. Obukhov and M. Rawiso, *Epl-Europhys Lett*, 2014, **106**.

20 J. M. Y. Carrillo and A. V. Dobrynin, *Macromolecules*, 2011, **44**, 5798.

21 A. Eich and B. A. Wolf, *Chemphyschem*, 2011, **12**, 2786.

22 T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.*, 1948, **70**, 2384.

23 V. R. Allen and T. G. Fox, *J. Chem. Phys.*, 1964, **41**, 337.

24 Y. Ohta, H. Murase, H. Sugiyama and H. Yasuda, *Polym. Eng. Sci.*, 2000, **40**, 2414.

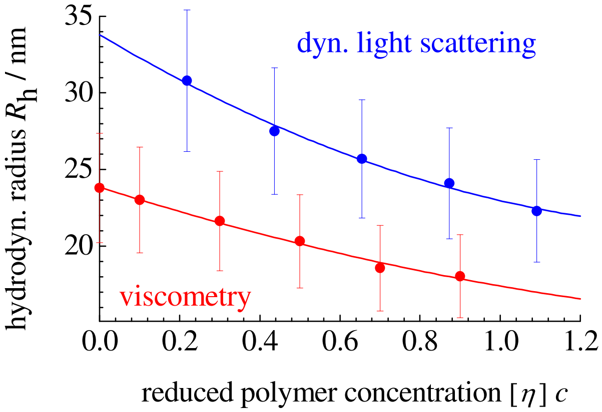
25 F. K. Herold and B. A. Wolf, *Mater. Chem. Phys.*, 1986, **14**, 311.

26 N. D. Koromilas, G. C. Lainioti, E. K. Oikonomou, G. Bokias and J. K. Kallitsis, *Eur. Polym. J.*, 2014, **54**, 39.

Graphical abstract

Polyelectrolytes in dilute solution: viscometric access to coil dimensions and salt effects

P. R. Suresha, Manohar V. Badiger and Bernhard A. Wolf



Viscometric and light scattering radii in water containing 0.25 mol NaCl per liter as a function of the reduced polymer concentration.