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Effective Size and Fractal Dimension of Polyelectrolytes Determined by Diffusion NMR

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Summary: Polyelectrolytes are macromolecules containing dissociable or charged groups on the main chain or in side groups. These charges are the basis of the water solubility of polyelectrolytes. The solution properties namely the conformation is determined by an interplay of thermodynamic and electric interactions. The electrostatic interaction is influenced by the ionic strength of the solution. As a measure of the effective size of the macromolecules the hydrodynamic radius is determined from the self-diffusion coefficient measured via pulsed- field gradient nuclear magnetic resonance. From variation of the hydrodynamic radius with molecular weight for each ionic strength, the fractal dimension has been determined for the example of poly(styrenesulfonate). With increasing ionic strength the fractal dimension, which describes the use of space for the fictitious growth of the molecule when increasing the molecular weight, increases. This implies a denser packing of the molecules in higher ionic strength.

Introduction

Polyelectrolytes are macromolecular compounds which are composed of repeat units with ionic or dissociable groups. The polyelectrolyte properties are determined by the chemical structure of the polymer chain, the charge density and strength and the arrangement of the charged groups. Solution properties, namely the polymer conformation, are determined by an interplay of thermodynamic and electrostatic interactions. Because of their water solubility polyelectrolytes are important compounds and are widely used. The interaction between dissolved polyelectrolytes and colloidal particles form the basis of numerous technical applications. They are needed for water purification and wastewater treatment, food processing and paper technology. Polyelectrolytes were also used manufacturing conductive coatings, sensor technology, cosmetics and membranes.

Although most applications involve polyelectrolytes in solutions, the solution properties particularly at dilute concentrations are not yet well understood. The fundamental model of polyelectrolytes in solution consists of polymer chains of charged monomers, an equal number of oppositely charged counterions and optionally additional salt ions of both charge signs. The electrostatic interactions between these charged species

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dominate the charge and conformational properties of the polyelectrolyte in the solution, whereby these properties also depended on the polyelectrolyte concentration, the chain length and the ionic strength of the solution. As charge and conformational properties both affect polyelectrolyte dynamics in solution, studying dynamic behaviour helps to elucidate factors influencing polyelectrolyte solution properties.

One possibility to obtain information on size and shape of molecules in solutions is the measurement of the self- diffusion coefficients. The diffusion is limited by the hydrodynamic friction. Based on the Einstein equation the friction coefficient can be derived from diffusion data. Nuclear magnetic resonance (NMR) is versatile tool for the investigation of structure and molecular dynamics in solids and liquids [1]. In addition to the commonly used scattering experiments, pulsed field gradient (PFG) NMR has been successfully established for making measurements of diffusion coefficients [2], which are derived from signal attenuation due to incoherent molecular displacement.

In the following the dependence of self- diffusion coefficient of low concentrated sodium poly(styrenesulfonate) solutions on salt concentration is investigated by PFGNMR. The additional variation of the molecular weight of the polymer provides insight into the density or the packing of the polyelectrolyte molecules in the solution under study.

Experimental Part

Spatial information is introduced to the NMR experiment by the application of additional space- dependent magnetic fields, so- called magnetic field gradients [3]. Time evolution of transverse magnetization leads to a phase modulation of the signal with a phase factor proportional to the evolution time. If the spins evolve under a magnetic field gradient, this phase modulation becomes space dependent. This is the effect of the first magnetic field gradient pulse in Fig. 1. The second gradient pulse of the same amplitude and duration would refocus this position- dependent phase modulation if the spins would experience the same local field during both pulses. During the time interval between the two gradient pulses Δ, spins may change their position, which means there is incomplete refocusing of the phase modulation. In the ensemble average not net phase modulation but an amplitude attenuation is observed. From this signal attenuation the diffusion coefficient is determined using the so-called Stejskal-Tanner [4] equation for the stimulated echo PFG experiment.

$$S(g)/S(0) = \exp[(-D_0 \gamma^2 g^2 \delta^2(\Delta-\delta/3))] \quad (1)$$

with γ the magnetogyric ratio, D_0 the one-dimensional self- diffusion coefficient, and g and δ the gradient strength and duration respectively. In the PFG NMR experiment diffusion is probed using a two- time correlation function, which means there is no information about the path of the molecule during the diffusion time [5].

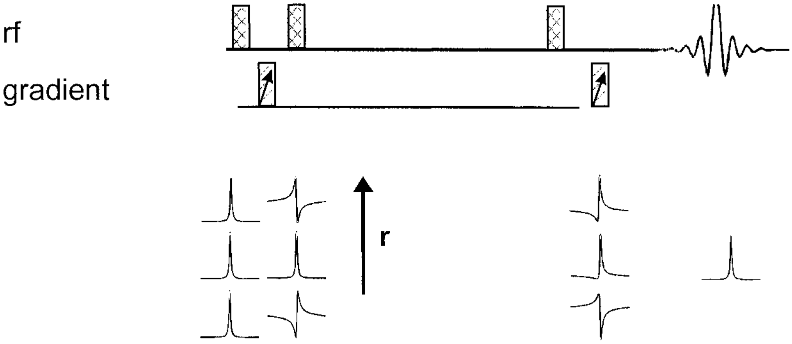

Figure 1: Schematic illustration of the pulsed field gradient stimulated echo NMR experiment. On the bottom schematically the signal phase for three locations is shown indicating the resulting signal attenuation.

The experiments have been performed on a Bruker AMX 300 NMR spectrometer operating at a Lamor frequency of 300 MHz for protons. The magnetic field gradients of a strength up to 1 T/m were generated by a commercial microimaging system (Bruker micro 2.5). All experiments were conducted at 20 °C. The diffusion coefficients were measured with the stimulated- echo pulse sequence. The three-pulse stimulated echo pulse sequence has the advantage, that the transverse relaxation time, which is comparably short for macromolecules, is effective for a shorter period of the experiment. The large magnetogyric ratio of protons grants both, high receptivity and a strong phase modulation effect of the gradient, resulting in a strong signal decay due to diffusion. Spectroscopic detection permits the evaluation of different species, that can be resolved in the spectrum [6].

A Stejskal-Tanner plot of the signal decay for NaPSS (M_W = 48.6 kg/mol) and residual HOD in D_2O with 0.02 mol/l NaCl is shown in Fig. 2. The experimental conditions are g_{max} = 1 T/m, δ = 3 ms and Δ = 150 ms. The self- diffusion coefficients, calculated from equation (1) are 3.2×10^{-11} m²/s for NaPSS (7.2 ppm) and 1.6×10^{-9} m²/s for HOD (4.8 ppm).

Sodium poly(styrenesulfonate), NaPSS, an anionic, linear, flexible and strong polyelectrolyte is chosen because of its availability as different molecular weight with narrow molecular weight distribution. Sodium poly(styrenesulfonate) of different molecular weights has been used as purchased from Fluka. The supplier- reported molecular weights (M_w), the polydispersity and the degree of sulfonation calculated from the molecular weights are listed in table 1. The powdered samples were evacuated for a minimum of 5 hours to obtain the dry weights, and to minimize subsequent the HOD formation which would limit the accessible concentration range. Polyelectrolytes were dissolved as 1 g/l (4.8×10^{-3} mol/l of monomer (monoM)) in D_2O (viscosity η_s= 1.24×10^{-3} Pas at 20°C). The chosen concentration of 1 g/l is well below the theoretical transition concentration between diluted and semidiluted solutions and interactions between the chains are negligible.

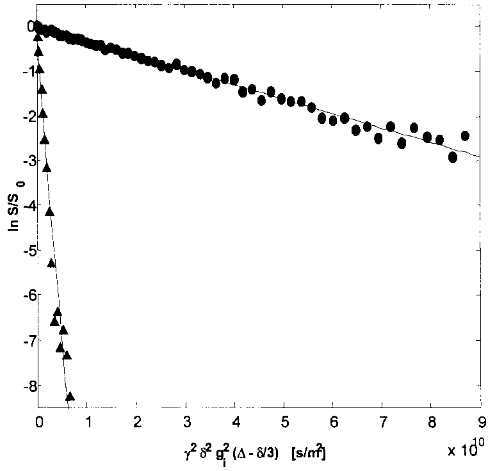

Figure 2: Stejskal-Tanner plot of echo signal decay for NaPSS-meta-phenyl-proton () and DHO-proton () in NaPSS 49 solution containing 0.02 mol/l NaCl. Solvent is D_2O.

Each of the polyelectrolyte solutions were prepared at least 3 days before measurement. Sodium chloride was also used as received and dried about 2 hours at 110°C.

Since the self- diffusion coefficients of polyelectrolytes in salt solutions up to 1 mol/l are quantified using a fixed polyelectrolyte concentration at constant temperature, the impact of electrostatic interactions upon the polyelectrolyte conformational properties is isolated from other contributions.

Table 1. Characteristics of sodium poly(styrenesulfonate) used in the experiments.

Name	M_W [kg/mol]	Polydispersity	Degree of sulfonation [%]
NaPSS 150	149	<1.2	85
NaPSS 77	77.4	<1.1	80
NaPSS 49	48.6	<1.2	95

Results

The self- diffusion coefficient of a polyelectrolyte is sensitive to its size and shape, which are determined by its conformation and hydrodynamic interactions with the solvent. For macromolecules the connection between molecular size and the diffusion coefficient is given through the Stokes-Einstein equation

$$D_o = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta R_h} \qquad (2)$$

where k_B is the Boltzmann constant, T is the temperature, η is the solvent viscosity and $f = 6\pi\eta R_h$ is the friction coefficient for a compact sphere in a viscous medium. The self-diffusion coefficient at constant temperature and solvent is therefore a measure of the average polyelectrolyte size. The hydrodynamic radius is the radius of a sphere that has the same hydrodynamic friction in the given medium.

The structure of polyelectrolyte chains also depends on the ionic strength of the solution and the charge density of the polyelectrolyte. Manning [7] showed, that if the charge density of the polyion is so high, that the distance between charges along the chain is shorter then a limiting value λ_B, the so- called Bjerrum length, counterion condensation occurs and reduces the effective charge of the chain. From the extension of the PFG experiment to electrophoresis NMR the effective charge of a polymer in solution is derived [8, 9]. The Bjerrum length, represents the distance over which the electrostatic energy between two neighbouring fixed charges is exactly compensated by the thermal energy $k_B T$. The ionic strength influences the electrostatic interaction range between macroion and counterions. The screening of charges due to the conductivity of the solution can be expressed by the Debye shielding length given as

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon k_B T}{2e^2 N_A I}} \qquad (3)$$

where ε_0 the vacuum permittivity, ε the solvent dielectric constant, k_B the Boltzmann constant, T the temperature, e the elementary charge, N_A the Avogadro number and I the ionic strength, defined as

$$I = \frac{1}{2}\sum_i z_i^{\,2} m_i \,. \tag{4}$$

The ionic strength contains both the concentration, the valence and the mobile part of the counterions. For a given dielectric constant the Debye length depends only on the square root of the ionic strength. The polyelectrolyte conformation depends on the electrostatic interactions between the charged groups on the macromolecule, therefore a dependence of the diffusion behaviour, probing the hydrodynamic size, on the ionic strength is expected as well.

Fig. 3 shows the self-diffusion coefficients of NaPSS (M_w = 48,6 kg/mol, c = 0,0048 mol/l) as a function of the added NaCl salt concentration.

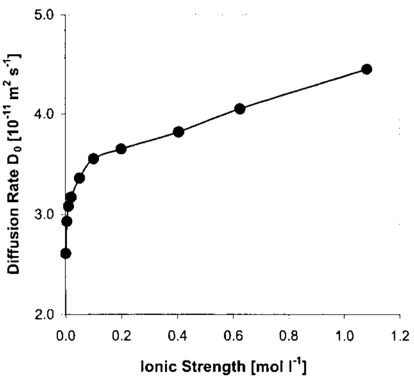

Figure 3: Self-diffusion coefficients of NaPSS 49 as a function of NaCl concentration expressed in terms of the ionic strength.

The diffusion coefficients increase rapidly initially and then more slowly with increasing salt concentration. The addition of salt enforces the electrostatic shielding and leads to a decrease of the radius of the polyelectrolyte chain and subsequent to faster diffusion. The other investigated substances, NaPSS 77 and NaPSS 150 behave in the same way. Because of the higher molecular weight the self- diffusion coefficients are lower in both, the salt-free and the salt-containing solutions compared with the NaPSS 49 compound. The self- diffusion coefficients decrease at constant ionic strength with the increasing in molecular weight. The calculated hydrodynamic radii rise with molecular weight, respectively, reflecting the increasing size of the molecule with an increasing number of repeat units.

The measured diffusion coefficients and the resultant calculated hydrodynamic radii display for each molecular weight a significant dependence on ionic strength and the Debye shielding length, respectively. In order to generalise the influence of the ionic strength on the molecular weight and the hydrodynamic radius the dependence of the hydrodynamic radius on the molecular weight was evaluated. From this dependence the fractal dimension of the molecules is derived [10]. This approach has previously been applied to the characterisation of the molecular packing of dendrimers in solution [11]. Figure 4 shows the fractal dimension as function of ionic strength and the Debye length respectively. With increasing ionic strength and thus resulting decreasing Debye length the fractal dimension increases. The fractal dimension describes the use of space for the fictitious growth of the macromolecule when increasing the molecular weight. So a higher fractal dimension reflects a denser packing of the molecule.

The increasing of the fractal dimension with increasing of the ionic strength may be explained by the fact, that the repulsion between monomers is increasingly screened by increasing the salt concentration. The chains contract even further from the condensation of counterions, reducing the effective charge density. [12].

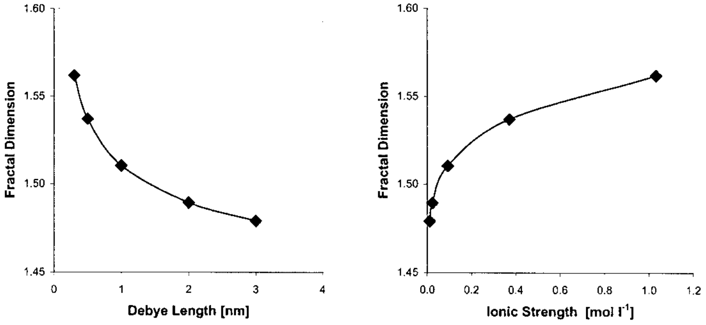

Figure 4: Fractal dimension as a function of NaCl concentration expressed in terms of Debye length (left) and ionic strength (right). The lines are guides to the eye only.

Conclusions

The impact of ionic strength upon the self- diffusion coefficient of sodium poly-(styrenesulfonate) at different molecular weights has been investigated by PFGNMR.

The ionic strength was changed by addition of the monovalent salt NaCl upon to 1 mol/l. Single- chain dynamics was isolated by using a low, constant, polyelectrolyte concentration. The hydrodynamic radii as a measure of the effective size of the macromolecules were determined from the Stokes- Einstein equation.

The self- diffusion coefficients increased with both, the decreasing of the molecular weight and the increasing salt concentration and attributed to the same effect, the decreasing of the hydrodynamic radius. The reasons of the decreasing however are very different. The molecular weight dependence of the hydrodynamic radius reflects the number of repeat units in the polymer. The decreasing of the hydrodynamic radius upon the addition of salt and increasing the ionic strength results from reduced electrostatic repulsion between charged groups.

From variation of the hydrodynamic radius with molecular weight for each ionic strength, the fractal dimensions for sodium poly(styrenesulfonate), a measure of the spatial distribution of the polyelectrolyte has been determined and correlated with the ionic strength. With increasing ionic strength, the fractal dimension increases. This implies a denser packing of the molecules in higher ionic strength.

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