

Effective charge of polyelectrolytes as a function of the dielectric constant of a solution

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Abstract

The combination of diffusion and electrophoresis NMR is applied to determine the effective charge of poly(styrene sulfonate) in solution. While electrophoresis NMR yields the electrophoretic mobility of the molecules in solution, the hydrodynamic friction is determined from diffusion NMR. From the force balance between electrostatic force and hydrodynamic friction, the effective charge of the molecule is determined free of any model. In the present study poly(styrene sulfonate) has been investigated in mixtures of water and methanol of varying composition. The lower dielectric constant in the mixtures with high methanol content results in a drastically reduced effective charge of the polyelectrolytes. The reduced effective charge along the polymer chain is the reason for a much more compact conformation of the polyelectrolyte, which is seen in a smaller hydrodynamic size of the molecule.

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1. Introduction

Polyelectrolytes have a number of applications to surface modification processes [1]. The deposition of polyelectrolyte layers and multilayers permits tailoring of surface properties such as charge and hydrophobicity. Polyelectrolytes are applied in the stabilization of suspensions and in the efficient flocculation of the solid content in waste water. They are used for the sorption of organic molecules and dyes from waste water as well [2].

Since the charges of polyelectrolytes are one of the driving forces for adsorption and binding, knowledge of the effective charges of polyelectrolytes in solution is important. The effective charge is determined by the nominal charge density on the polymer, the degree of dissociation, and the degree of counterion condensation [3]. Since poly(styrene sulfonate) is a strong polyelectrolyte, the acid groups are completely dissociated in aqueous solution in the pH ranges of interest. The nominal charge density is given by the structure of the polymer with

a charge–charge separation of 2.5 Å and a given degree of sulfonation of about 90%, as determined by chromatography. The remaining variable is the fraction of condensed counterions, which has a significant influence on the number of charges available depending on the solvent properties [4]. The fraction of condensed counterions is determined by the energy required for a counterion to move away from the polyelectrolyte, escaping the electrostatic field of the polyelectrolyte charges, which is lowered by counterions compensating for a fraction of the charges on the polymer. Condensed counterions move with the macromolecule but may exchange with free counterions over longer times [5].

For the determination of the effective charge, pulsed-field-gradient (PFG) NMR has been applied. In the stimulated-echo pulsed-field-gradient NMR experiment, the coefficient of the self-diffusion of the molecule in solution is determined from the signal attenuation as a function of the magnetic field gradient applied [6,7]. From the diffusion coefficient, the coefficient of velocity-proportional hydrodynamic friction is determined according to Einstein's formula [8]. From the friction coefficient, the hydrodynamic radius may be calculated following the Stokes–Einstein formula [9,10], which gives a measure for the space occupied by the molecule in the solution [11,12].

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If a DC electric field is applied during the PFG NMR experiment, charged molecules will move coherently along the field lines [13–15]. This coherent motion results in phase modulation of the NMR signal as a function of either the strength of the magnetic field gradient or the electric field strength. If only the electric field strength is varied while all other parameters are kept constant, effects of relaxation and the superimposed diffusion of the molecules do not influence the signal. Thus even slow coherent motion resulting in displacements comparable to those resulting from diffusion is resolved [16,17].

Since the time scale of the NMR experiment is on the order of tens of milliseconds, a steady state with a constant velocity is observed. Constant velocity results from a balance between the force of the electric field on the effective charge of the molecule and the velocity-dependent hydrodynamic friction. From this force balance the number of charges z is calculated to be

$$z = \frac{k_B T \mu}{e D} \quad (1)$$

The resulting number, for most polyelectrolytes, is significantly lower than the nominal number of charges calculated from the number of repeat units. In the present study, the effective charge of poly(styrene sulfonate) has been investigated in mixtures of methanol and water to study the influence of variations of the dielectric constant of the solvent on the effective charge of the polyelectrolyte.

2. Experimental

2.1. Materials

Sodium poly(styrene sulfonate) of molecular weight 77 kg/mol (PSS77) was purchased from Fluka. It was tried under vacuum and used without further treatment. Tetradeuteromethanol (CD_3OD , 99.8%) and deuterated water (D_2O , 99.95%) were obtained from Deutero GmbH. Deuterated solvents were used to minimize the residual proton signals of the solvent and to facilitate measurement of low polyelectrolyte concentrations. For all experiments, a concentration of 1 g/L PSS77 (5 mmol/L (monomer)) in mixtures of different volume fractions (v/v %) has been used. Samples were prepared from a stock solution of 10 g/L PSS77 in CD_3OD with 2% v/v deuterated water upon addition of corresponding aliquots of the solvents. The viscosity and dielectric constants for the mixtures of D_2O and CD_3OD are depicted in Figs. 1 and 2, respectively. PSS77 is insoluble in pure methanol. Preparation of samples was performed immediately before measurements, avoiding intrusion of water into the hygroscopic solvents.

2.2. NMR measurements

All experiments were conducted at 20 °C. Diffusion NMR experiments were performed on a Bruker Avance 500 NMR spectrometer operating at a Larmor frequency of 500 MHz for protons and equipped with a Diff30 probe with a z -gradient providing magnetic field gradients up to 11.6 T/m. A stimulated-echo pulse sequence has been applied to measure diffusion.

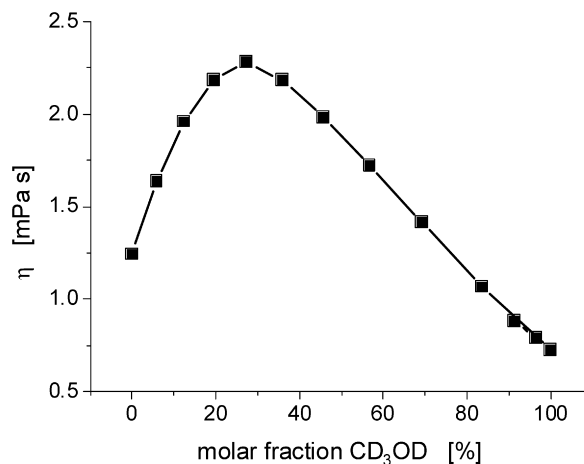


Fig. 1. Viscosity for deuterated methanol–water mixtures at 20 °C. The values for methanol–water mixtures have been taken from Refs. [21,22] and have been converted according to [23] to values of deuterated mixtures.

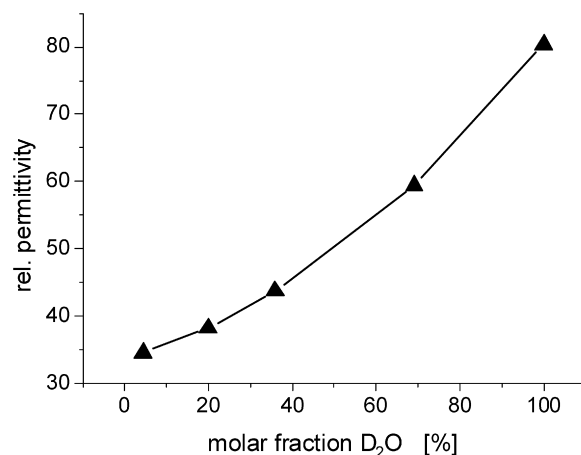


Fig. 2. Dielectric constants for methanol–water mixtures at 20 °C. The values were obtained by regressing data in Ref. [24]. The dielectric constants for tetradeuteromethanol and deuterated water are almost identical [23].

Gradients were incremented linearly in 64 steps. The gradient pulse duration δ , diffusion time Δ , and starting gradient strength were varied for each sample in order to get a small signal of the residual solvent protons at the first gradient strength step and a minimum signal of the PSS at the last. The gradient pulse duration δ was varied between 0.7 and 1.5 ms, the diffusion time Δ between 10 and 20 ms, and the first gradient strength between 0.5 and 1 T/m, respectively.

The electrophoresis experiments were performed on a Bruker Avance 300 NMR spectrometer operating at a Larmor frequency of 300 MHz for protons, equipped with a micro 2.5 microimaging accessory providing magnetic field gradients up to 1 T/m.

The electrophoresis NMR system was in-house built [5]. The electrophoresis cell was a U-shaped tube with the NMR coil on one side of the U. A pair of platinum electrodes were placed on top of the U-tube, permitting gaseous products of possible electrode reactions to escape without disturbing the NMR experiment. The platinum electrodes were connected to a custom-made DC amplifier producing a maximum of ± 1000 V [18],

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