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## LETTER TO THE EDITOR

# Dynamics of Na<sup>+</sup>-polystyrene sulphonate in solution at low ionic strength

F Grüner, W P Lehmann, H Fahlbusch and R Weber

Fakultät für Physik, Universität Konstanz, Bücklestrasse 13, 7750 Konstanz, FRG

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**Abstract.** The dynamics of Na<sup>+</sup>-polystyrene sulphonate (Na<sup>+</sup>PSS) (MW = 10<sup>5</sup>) in water of low ionic strength was investigated by photon correlation spectroscopy. The cooperative diffusion coefficient  $D_{\text{eff}}$  obtained from the first cumulant was measured in a concentration range of five decades. The lowest concentrations are in the dilute regime. In the semidilute regime, that is for concentrations greater than the overlap concentration  $c^* \approx 3 \times 10^{-7}$  monomers  $\text{\AA}^{-3}$ , the cooperative diffusion coefficient follows a power law  $D_{\text{eff}} \sim c^{0.52 \pm 0.02}$  which is in good agreement with theoretical predictions for polyelectrolytes. At very high concentrations,  $c > c^{**} \approx 3 \times 10^{-5}$  monomers  $\text{\AA}^{-3}$ , a new regime, which we call the concentrated regime, is observed which shows a constant  $D_{\text{eff}}$ . This behaviour may be explained by a scaling law, which takes the electrostatic persistence length as the fundamental parameter.

## 1. Introduction and experimental procedure

As expressed by Hayter *et al* (1980), polyelectrolyte solutions without added salt constitute one of the most mysterious states of condensed matter. To increase the insight into this 'mysterium', we have performed a photon correlation spectroscopy study of Na<sup>+</sup>-PSS solutions in water of low ionic strength. The main purpose of these investigations was to obtain information on the conformation of the polyions and to test the predictions of the theory on the scaling behaviour of polyelectrolytes (de Gennes *et al* 1976, Odijk 1979). To our knowledge, all experiments on Na<sup>+</sup>-PSS carried out so far were either in solutions with added salt (e.g. Koene *et al* 1980) or at concentrations greater than  $c^{**}$  (e.g. Hayter *et al* 1980, Williams *et al* 1979).

However, as we will show, at the concentration  $c^{**}$  the semidilute regime ends, and the concentrated regime begins, where the cooperative diffusion coefficient shows a different behaviour.

We used Na<sup>+</sup>-PSS of molecular weight 10<sup>5</sup> supplied by Serva, Heidelberg. It was dissolved in water which was deionised carefully (18 M $\Omega$ cm) and filtered by a Millipore filter of pore size 0.022  $\mu$ . Thus virtually no contamination by dust from the solvent was encountered. At concentrations of 10<sup>-4</sup> g cm<sup>-3</sup> and lower, we filtered the prepared solutions, which exhibit a very low intensity of scattered light, again with a Millipore filter of pore size 0.022  $\mu$  to remove any remaining particles which may disturb the measurements at these very low concentrations. This procedure may change the concentration of the samples. However, by comparing the total scattered intensities before and after filtering, the changes in concentration were estimated to be negligible.

The concentrations given were determined by weighing the ingredients and have an uncertainty of less than 5%.

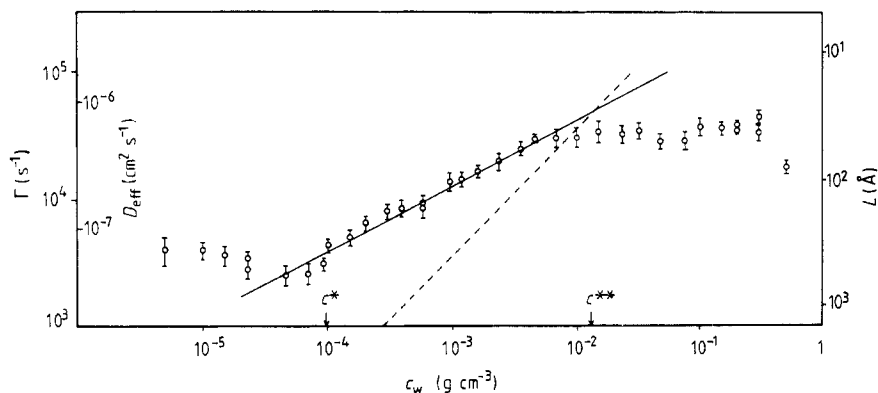
The experiments were performed using 50 to 200 mW of Ar-laser light with a wavelength of 488 nm. The samples were contained in cylindrical quartz tubes of 6 mm inner diameter immersed in a temperature stabilised ( $T = 298 \pm 0.5$  K) bath of glycerine. The intensity (homodyne) correlation function was measured with a 4000 channel quasi real time autocorrelator (Lehmann 1981). The data analysis was done by calculating the field autocorrelation function by means of the Siegert relation

$$\frac{\langle E(\tau)E^*(0) \rangle}{\langle I \rangle} = \left( \frac{\langle I(\tau)I(0) \rangle}{\langle I \rangle^2} - 1 \right)^{1/2}.$$

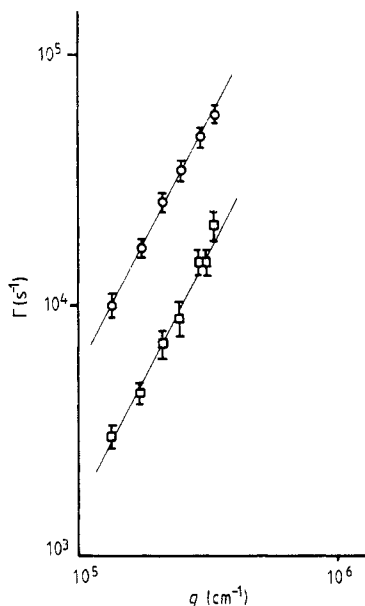
This function was then fitted to a sum of exponentials using the Discrete program due to Provencher (1976).

## 2. Results

Most of the data were conveniently fitted by the sum of two exponentials. The deviations from a single exponential behaviour were smallest at high concentrations and largest at low concentrations. From the data of the fit we calculated the first cumulant  $\Gamma$ . In this paper we will deal only with this quantity, which gives the cooperative diffusion coefficient of the sample. The concentration dependence of  $\Gamma$  for  $90^\circ$  polarised scattering (wavevector  $q = 2.43 \times 10^5 \text{ cm}^{-1}$ ) is shown in figure 1. The error bars quoted are the 65% confidence intervals given by the fit procedure. It may be seen that the concentration range covered may be divided into three regions, which we associate with the dilute, semidilute and concentrated regimes. Since the experiments in the dilute regime are extremely difficult because of the low scattering intensities, we have not investigated the wavevector dependence of the cumulant in this regime up to now. In the semidilute and concentrated regimes the cumulant follows a  $q^2$  law, as may be seen from figure 2. To check whether the dynamics of the highly concentrated



**Figure 1.** Concentration dependence of the first cumulant  $\Gamma$  or the cooperative diffusion coefficient  $D_{\text{eff}}$  respectively (left scale) for  $q = 2.43 \times 10^5 \text{ cm}^{-1}$  ( $\lambda = 488 \text{ nm}$ ,  $\theta = 90^\circ$ ) at  $T = 298 \text{ K}$ . The full line is the fitted concentration dependence of the screening length  $\xi \sim c^{-0.521}$  in the semidilute regime. The broken line is the calculated electrostatic persistence length  $L_e$  (refer to right scale where  $L = kT/D_{\text{eff}}6\pi\eta$ ).



**Figure 2.** Wavevector dependence of the first cumulant  $\Gamma$  for a sample in the semidilute ( $\square$ :  $1.0 \times 10^{-3} \text{ g cm}^{-3}$ ) and in the concentrated ( $\circ$ :  $4.6 \times 10^{-2} \text{ g cm}^{-3}$ ) regimes. The solid lines correspond to  $\Gamma \sim q^2$ .

samples is of purely diffusive character, the temperature dependence of the cumulant was also measured for some concentrations. It is seen from figure 3 that, even at concentrations of  $c_w = 0.3 \text{ g cm}^{-3}$ , the data agree with the expected behaviour for a solution in water, where the solvent viscosity  $\eta_w(T)$  determined the friction and hence the diffusion coefficient:

$$\Gamma \sim D_{\text{eff}} \sim kT/\eta_w(T).$$

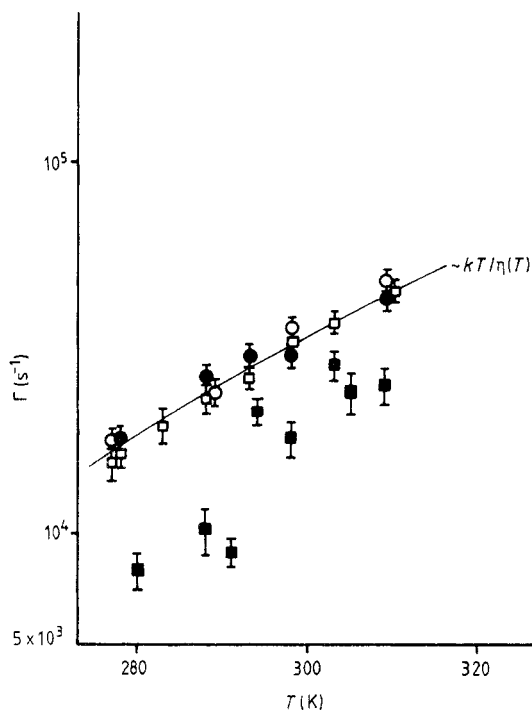
Only the highest concentrated sample,  $c_w = 0.5 \text{ g cm}^{-3}$ , shows a significant deviation from this behaviour, indicating that this sample may no longer be regarded as a simple solution of  $\text{Na}^+$ -PSS in water.

### 3. Discussion

The  $\text{Na}^+$ -PSS molecule of molecular weight  $10^5$  consists of  $N = 480$  monomers of length  $a = 2.5 \text{ \AA}$  (contour length  $l = 1200 \text{ \AA}$ ). Each monomer carries one  $\text{Na}^+$  ion, which may dissociate. Since the Bjerrum length  $Q = 7 \text{ \AA}$  is greater than  $a$ , counterion condensation has to be taken into account (Manning 1969). This leads to an electrostatic persistence length of (Odijk 1978)

$$L_e = 1/4 Q \kappa^2 = 1/16 \pi Q a c.$$

For the evaluation of the Debye-Hückel parameter  $\kappa$ , it was assumed that all counterions emerge from the polyions only.  $c$  is the monomer concentration, which is connected with the concentration per weight by the relation  $c = 2.9 \times 10^{-3} (\text{monomers cm}^{-3} \text{ g}) c_w$ .



**Figure 3.** Temperature dependence of the first cumulant  $\Gamma$  of various samples in the concentrated regime. The line is calculated with the viscosity of pure water.  $\bullet$ :  $4.6 \times 10^{-2} \text{ g cm}^{-3}$ ;  $\circ$ :  $1.5 \times 10^{-1} \text{ g cm}^{-3}$ ;  $\square$ :  $3.0 \times 10^{-1} \text{ g cm}^{-3}$ ;  $\blacksquare$ :  $5.0 \times 10^{-1} \text{ g cm}^{-3}$ .

### 3.1. Dilute regime

In the dilute regime ( $c_w < 10^{-4} \text{ g cm}^{-3}$ ) the electrostatic persistence length is  $L_e > 3900 \text{ \AA}$  which is greater than the contour length  $l = 1200 \text{ \AA}$ . Therefore no gaussian coil behaviour is expected. Indeed, a diffusion coefficient of  $D_d = 6.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  is measured for the three lowest concentrations  $c_w = 5.0 \times 10^{-6}$ ,  $1.0 \times 10^{-5}$  and  $1.5 \times 10^{-5} \text{ g cm}^{-3}$ . This would yield a hydrodynamic radius of  $R_H = 360 \text{ \AA}$  according to the Stokes–Einstein relation, and a mean end-to-end distance (Flory radius) of about  $R_F = 890 \text{ \AA}$ . These numbers are clearly too large for a gaussian coil with contour length  $l = 1200 \text{ \AA}$ . If, however, the molecules have an elongated conformation, the Stokes–Einstein relation will no longer hold. Taking the formula for the friction coefficient of prolate ellipsoids (Perrin 1934) with half axes  $600 \text{ \AA}$  and  $6 \text{ \AA}$ , which would describe the totally stretched molecule, a diffusion coefficient of  $9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  is estimated in reasonable agreement with the experiment.

This agreement is a hint to a stretched conformation, although two questions remain open regarding the dilute regime. The first question is the polydispersity, which will influence the correlation function in the dilute regime. Since in this paper we are dealing with the first cumulants only, we will obtain the average diffusion coefficient and the average radius. Therefore this problem should not alter the conclusion for the conformation. The second open question is the question of intermolecular interactions in the dilute phase. These interactions could alter the cumulants severely (see e.g. Brown *et al* 1975, Gr uner and Lehmann 1979); hence further experiments are needed for clarification, and are on the way.

### 3.2. Semidilute regime

The most sensitive measure for the conformation is the overlap concentration  $c^*$  at which the semidilute regime starts. It is given, apart from factors of order unity, as

$$c_{\text{Coil}}^* \approx N/R_F^3$$

in the case of gaussian coils (de Gennes 1979) and as

$$c_{\text{Rod}}^* \approx N/l^3$$

for a fully elongated molecule. Assuming a statistical segment length of  $44 \text{ \AA}$  as was given by Koene *et al* (1980) for  $\text{Na}^+$ -PSS in 0.01 molar salt solution, the Flory radius would be  $R_F = 320 \text{ \AA}$  and the overlap concentration would be  $c_{\text{Coil}}^* = 5 \times 10^{-3} \text{ g cm}^{-3}$ . For a smaller statistical segment length, the overlap concentration would be even higher. On the other hand, for a fully extended molecule of length  $l = 1200 \text{ \AA}$  the overlap concentration is calculated to be  $c_w^* = 9.6 \times 10^{-5} \text{ g cm}^{-3}$ , which is in excellent agreement with the experimental observation. This is a strong argument, which supports our assumption of a rod-like molecule in the dilute regime.

Above the overlap concentration  $c^*$ , the cooperative diffusion coefficient is given by (de Gennes 1979)

$$D_{\text{eff}} = kT/6\pi\eta\xi$$

where  $\xi$  is the screening length, that is the mean distance between entanglements. Therefore we expect the cumulant to vary according to the inverse of the screening length. Fitting the 14 data points in the semidilute regime between  $c_w = 1.0 \times 10^{-4} \text{ g cm}^{-3}$  and  $7 \times 10^{-3} \text{ g cm}^{-3}$  to a simple power law, we obtain the result  $\xi = 3.01 \times c_w^{-(0.521 \pm 0.024)} (\text{\AA})$  (full line in figure 1). This is different from the exponent observed in polymers  $\xi \sim c^{-0.7}$  (Adam and Dalsanti 1977), and is in excellent agreement with the scaling theories of de Gennes *et al* (1976) and Odijk (1979) who predicted for polyelectrolytes a power law according to

$$\xi = (ac)^{-1/2}.$$

Our observations are the first experimental proof for these scaling law predictions.

### 3.3. Concentrated regime

There exists a third concentration regime at concentrations higher than  $10^{-2} \text{ g cm}^{-3}$ . In this concentrated regime we observe an essentially constant  $D_{\text{eff}}$ . A transition from the semi-dilute to another regime was predicted by Odijk (1979) at

$$c^{**} \approx 0.04/4\pi Q^2 a.$$

In our case  $c^{**}$  is calculated from this formula to be  $9 \times 10^{-3} \text{ g cm}^{-3}$ , which is in good agreement with the experimental observation. However, above  $c^{**}$  Odijk predicts  $\xi \sim c^{-3/8}$  and  $\xi \sim c^{-5/8}$  respectively, which is obviously not observed. Therefore, we believe that this transition is connected with the transition to another length scale. This is suggested by the left part of figure 1 where the screening length  $\xi$  in the semidilute regime (full line) and the persistence length calculated according to (1) (broken line) are shown together with the experimental data (refer to right scale). It is seen that at a concentration of  $c_w^{**} = 1.3 \times 10^{-2} \text{ g cm}^{-3}$  the experimental  $\xi$  and the calculated  $L_e$  are

the same. If we force the exponent of the experimental  $\xi$  to be  $-0.5$ , the condition  $\xi(c^{**}) = L_e(c^{**})$  yields

$$0.30(ac^{**})^{-0.5} = (16\pi Qac^{**})^{-1} \quad c^{**} = 4.4 \times 10^{-3}/Q^2a$$

which apart from factors of order unity, is the same result as that given by Odijk (1979) from different points of view.

Up to the concentration  $c^{**}$  all scaling laws are based on the assumption that the contour length  $l$  is the basic length scale, and neither the monomer length nor something like a mean end-to-end distance plays a role, or, in a more intuitive description, that the molecule is always more or less stretched between two entanglements. Above the concentration  $c^{**}$ , the electrostatic persistence length becomes smaller than the screening length (mean distance between entanglements). Therefore the molecule is no longer stretched. If we assume that the basic length now is the electrostatic persistence length and that the screening length depends on the concentration by a power law

$$\xi \approx L_e(C/c^{**})^\mu$$

we end up with

$$\xi \sim Q^{2\mu-1} a^{\mu-1} c^{\mu-1}.$$

We now argue that  $\xi$  should not depend on the monomer length  $a$  as long as  $a < Q$  and  $a < L_e$ . This leads to an exponent of  $\mu = 1$  and, including the prefactors, to

$$\xi \approx 4.5Q = 32 \text{ \AA}$$

independent of  $c$ .

Since the effects of the intrinsic persistence length have been neglected and only the prefactor of the scaling law for  $\xi$  in the semidilute regime has been taken from the experiment, the agreement is surprisingly good. The result should hold for all polyelectrolytes as long as  $a < Q$  and the ionic strength of the solution is only determined by the counterions emerging from the polymer.

Above  $c_w = 0.1 \text{ g cm}^{-3}$  deviations from the concentration-independent behaviour are observed. These deviations occur since  $L_e$  becomes of the order of  $a$  and the intrinsic persistence length should be taken into account. Secondly, the simple theory of counterion condensation is probably no longer a good approximation at these high concentrations.

#### 4. Conclusions

The dynamics of  $\text{Na}^+$ -PSS in water without added salt was investigated in the dilute, semidilute and concentrated regimes. The results so far obtained give strong evidence that the conformation of the polyion is rod-like at low concentrations (dilute regime) and stays extended between entanglements in the semidilute regime. The overlap concentration  $c^*$  and the scaling exponent of the screening length for a polyelectrolyte at low ionic strength were determined for the first time and agree well with the theoretical predictions. A second crossover concentration  $c^{**}$  was observed where the molecule starts to bend, that is, where the electrostatic persistence length  $L_e$  becomes smaller than the screening length  $\xi$ . The concentrated regime has an essentially

constant screening length, which may be explained by scaling arguments. The question of intermolecular interactions in the dilute regime clearly needs further investigations, which are on the way.

### Acknowledgments

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### References

- Adam M and Dalsanti M 1977 *Macromolecules* **10** 1229  
Brown J, Pusey P N, Goodwin J W and Ottewill R H 1975 *J. Phys. A: Math. Gen.* **8** 664  
de Gennes P G 1979 *Scaling Concepts in Polymer Physics* (Ithaca: Cornell University Press)  
de Gennes P G, Pincus P, Velasco R M and Brochard F 1967 *J. Physique* **37** 1461  
Grüner F and Lehmann W 1979 *J. Phys. A: Math. Gen.* **12** L303  
— 1980 in *Light Scattering in Liquids and Macromolecular Solutions* (New York: Plenum)  
Hayter J, Janninck G, Brochard-Wyart F and de Gennes P G 1980 *J. Physique Lett.* **41** L451  
Koene R S, Smit H W J and Mandel M 1980 *Chem. Phys. Lett.* **74** 176  
Lehmann W P 1981 *J. Phys. E: Sci. Instrum.* **14** 709  
Manning G S 1969 *J. Chem. Phys.* **51** 924  
Odijk T 1978 *J. Polym. Sci., Polym. Phys. Ed.* **16** 627  
— 1979 *Macromolecules* **12** 688  
Perrin F 1934 *J. Phys. Radium* **5** 497  
Provencher S W 1976 *J. Chem. Phys.* **64** 2772  
Williams C E *et al* 1979 *J. Polym. Sci., Polym. Letters Ed.* **17** 379