Sedimentation behaviour in semidilute solutions of polyelectrolyte

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Introduction

Polyelectrolytes are polymers having one or more ionizable groups per monomeric unit. In solution, they show features of both electrolytes and linear polymers. It is frequently argued that in dilute solution, in absence of salt, the polyions are extended and assume a rod-like conformation due to electrostatic repulsion, but that they contract progressively when salt is added, or when the polyelectrolyte concentration increases. In this latter case where the concentration increases, polyelectrolytes have more of less coiled conformations.

A number of recent investigations, both theoretical and experimental, have been devoted to the study of conformational problems in semidilute polyelectrolyte solutions. However, there is a lack of work dealing with transport properties in semidilute solutions.

The principal aim of the present investigation is to study the concentration dependence of the sedimentation coefficient in semidilute polyelectrolyte solutions at varying ionic strengths. The sedimentation velocity measurements have been carried out in aqueous solutions of sodium poly(styrene sulphonate) (NaPSS), both with and without added salt. The results will mainly be discussed within the framework of recent scaling law hypotheses[1-3].

Experimental

A narrow molecular weight distribution standard sample of sodium poly(styrene sulphonate) (NaPSS) (Pressure Chemical Company, Pittsburgh, Pa.) characterized by $\bar{M}_w = 1.06 \times 10^6$ and $\bar{M}_w/\bar{M}_n \approx 1.1$ (manufacturer's data for lot No. 17), was used.

An elementary analysis showed that the sample contained 14.11% S and less than 0.12% Cl. The sulphur content indicated that the degree of sulphonation is 0.91 for this sample. Sodium chloride (NaCl) (Merck A.G.) was of p.a. grade and the specific conductivity of the distilled water used was less than $0.9 \cdot 10^{-4}\ \Omega^{-1}\ \mathrm{m}^{-1}$.

Prior to preparation of the solutions both NaPSS and NaCl were dried in vacuum at about 50°C for 12 h. All solutions were prepared by weighing. The polyelectrolyte concentration (mass/volume), c, was calculated from the weight fraction of solute, w, and the corresponding solution density, ρ, according to the relation $c = \rho w$; numerical values of ρ were taken from data published elsewhere[4].

Sedimentation experiments were performed at 54000 rpm in an MSE analytical ultracentrifuge (Centriscan 75) equipped with a temperature controlling unit and a Schlieren optical system. The cell consisted of 20 mm single sector epoxy resin centre pieces with quartz windows. The measurements were made at 25°C with three different salt concentrations (0 M, 0.002M and 0.1M).

The measurements and the calculation of the sedimentation coefficients were in accordance with the principles discussed previously[5].

Results and discussion

Recently, Odijk[3] derived scaling relations for semidilute polyelectrolyte solutions, both with and without added salt, by using recent scaling theories of non-ionic polymer solutions, and the theory of the electrostatic persistence length, L_e. The basic notions are the existence of an electrostatic persistence length and the concept of local cylindrical geometry.

Polyelectrolyte solutions with salt. In the theory of Odijk[3] the polyion can be viewed as a wormlike chain of contour length l and bare persistence length, L_p, bearing elementary charges (q) which interact via a Debye–Hückel potential with screening length κ^{-1}. Each chain bears P charged beads equidistant along the chain, and the beads are separated by the contour distance $A = lP^{-1}$.

The charges stiffen the chain locally, and a measure of the electrostatic contribution to the stiffness of the polyelectrolyte chain is the electrostatic persistence length, L_e, defined by

$$L_e = Q/4\kappa^2 A^2 \lambda^2 \tag{1}$$

Here $Q \equiv q^2/DkT$ represents the Bjerrum length with k the Boltzmann constant, T the absolute temperature and D the dielectric permittivity of the solvent. The charge-density parameter λ is unity for $A > Q$ but $\lambda = Q/A$ for $A \leq Q$. For the present system $A = 2.5\text{Å}$ and $Q = 7\text{Å}$, i.e. $A < Q$ and equation 1 is modified to

$$L_e = 1/4Q\kappa^2 \tag{2}$$

The length scale κ^{-1} may be expressed as

$$\kappa^2 = 8\pi QI \tag{3}$$

with I the ionic strength of the solution due to added 1:1 electrolyte.

The total persistence length L_t consists of an intrinsic part, L_p, and an electrostatic part, L_e, and is given by

$$L_t = L_p + L_e \tag{4}$$

For the present system $L_p \approx 10\text{Å}$.

A semidilute solution of polyelectrolyte may be visualized as a succession of 'blobs' each of size, ξ, the screening length, which should be independent of the contour length l but dependent on the polyelectrolyte concentration, c. By using a standard scaling procedure Odijk formulated the following relation for ξ in the semidilute range

$$\xi \sim L_t^{-1/4} \kappa^{1/4} (Ac)^{-3/4} \tag{5}$$

Brochard and de Gennes[6] have shown that for non-ionic polymer solutions in the semidilute regime the sedimentation coefficient, s, is proportional to $c\xi^2$ if the

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chains are infinitely long. If we adopt the relation $s \sim c\xi^2$ and insert equation 5 we obtain

$$s \sim L_t^{-1/2}\kappa^{1/2}A^{-3/2}c^{-1/2} \qquad (6)$$

In the semidilute regime where the polyelectrolyte concentration is fairly high, the ionic strength I (see equation 3) has to be corrected for[7] the contribution from the small ions originating from the polyelectrolyte. By introducing the simple condensation approach the ionic strength I may be calculated from the relation

$$I = c_s + c/2\lambda M_{mon} \quad (M_{mon} = 206.2\cdot10^{-3}\,\mathrm{kgmol}^{-1}) \qquad (7)$$

where c_s is the salt concentration (1:1 electrolyte), c is the polyelectrolyte concentration, and λ is the charge density parameter ($\lambda = 2.8$ in the present study). As a consequence κ and hence L_e (and L_t) are concentration dependent. Therefore, it is convenient to introduce an 'effective' sedimentation quantity, $\bar{S}$, given by

$$\bar{S} \equiv \frac{s}{L_t^{-1/2}\kappa^{1/2}} \sim A^{-3/2}c^{-1/2} \qquad (8)$$

Figure 1a shows a log–log plot of $\bar{S}$ *versus* c for NaPSS solution of different salt concentrations. The $\bar{S}$ values have been determined from the sedimentation coefficients by means of equation 8 using equation 7 in the calculation of κ (equation 3) and L_e (equation 2). The data for the system with the highest salt concentration ($c_s = 0.1$M) indicate a sedimentation behaviour reminiscent of that reported[8] for non-ionic polymers in aqueous solutions. The concentration $c^* = 1/[\eta]$ (where $[\eta]$ is the limiting viscosity number), which has previously[9,10] been recognized for solutions of non-ionic polymers to separate the dilute and semidilute regimes in sedimentation experiments, is indicated by a vertical broken line in *Figure 1a*. This crossover concentration corresponds to a situation where the polymers coils show incipient overlap. In the semidilute regime the data for the system with $c_s = 0.1$M may be represented by a straight line with a slope of -0.64. This value diverges from that predicted by equation 8. However, this divergence is probably associated with an effect of the Weill-des Cloizeaux[11] type, in a similar way as that observed in sedimentation experiments for solutions of non-ionic polymers[10,12].

In the case of low salt concentration ($c_s = 0.002$M) the picture is more complicated. There is a 'hump' in the curve located approximately at 3 kgm^{-3}. This anomaly is similar to that observed in absence of salt (see *Figure 1b*). The points for concentrations well above 3 kgm^{-3} may be represented by a straight line with a slope of -0.8. However, it should be noted that equations 5 and 8 are derived with the restriction of excess salt concentration, which is not fulfilled in this case.

Polyelectrolyte solutions without salt. Investigations on polyelectrolyte solutions without added salt have shown that these systems are rather complex[13–15]. On the theoretical front the situation is obscure, especially when it concerns dynamical properties. Some scaling relations[1–3] have been formulated for static properties in semidilute polyelectrolyte solutions without salt, but these relations are based on some uncertain conjectures.

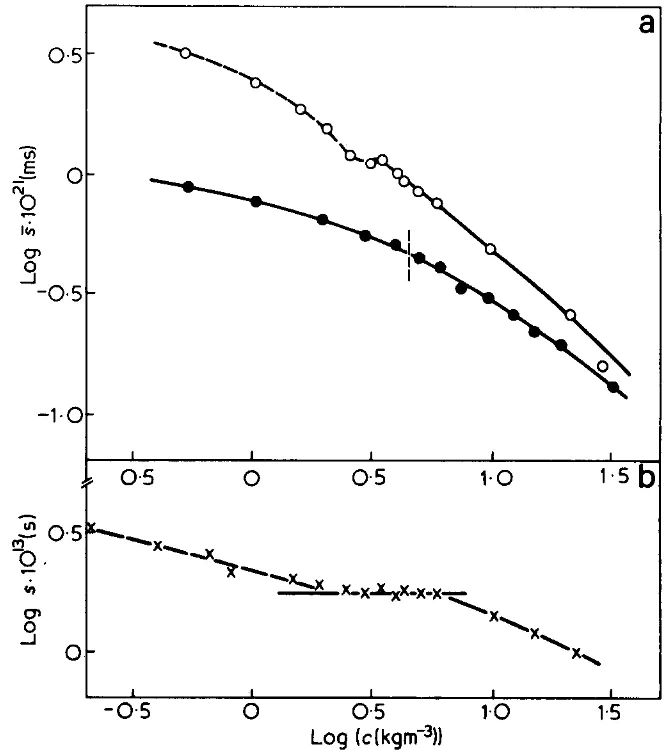

Figure 1 (a) Log–log plot of $\bar{S}$ (equation 8) *versus* c for the system NaPSS/H_2O in presence of salt: (○), $c_s = 0.002$M; (●), $c_s = 0.1$M. The vertical broken line indicates the cross-over concentration $c^* = 1/[\eta]$ (see text). (b) Log–log plot of sedimentation coefficient, *s*, *versus* *c* for the system NaPSS/H_2O in absence of salt

In a polyelectrolyte solution without added salt the chains are extended and the overlap concentration c^* may be estimated from a relation given in ref 3

$$c^* \approx \frac{M}{16\pi N_A Q A l} \qquad (9)$$

where M is the molar mass and N_A is the Avogadro constant. For the present system $c^* = 0.03$ kgm^{-3}. The experimental concentrations range from 0.2 to 30 kgm^{-3}; thus far above the overlap concentration.

Figure 1b shows a log–log representation of the sedimentation coefficient, *s* vs *c* for NaPSS solutions without added salt. The resulting curve displays a complex behaviour. Initially, *s* decreases with concentration; at higher concentrations the value of *s* is practically independent of *c*. At still higher concentrations *s* decreases again. The origin of these peculiar features is not established, but some tentative speculations may be given. The first part of the curve may represent a situation where the extended polyions reorient in such a way that an alignment of the molecules occurs. The plateau-like region probably indicates incipient 'entanglements' effects. At higher concentrations these effects will progressively increase in importance. Furthermore, at higher concentrations it is likely that the polyelectrolytes have more or less coiled conformations.

In this context it is interesting to note that in the regime $c \gg c^*$, theoretical models[1–3] give the following expression for the screening length.

$$\xi \sim (Ac)^{-1/2} \qquad (10)$$

By inserting relation 10 in the relation $s \sim c\xi^2$, the sedimentation coefficient should be independent of concentration. Perhaps this theoretical prediction is reflected in the plateau-like regime in *Figure 1b*.

Sedimentation experiments with the aim of more systematically studying the influence of molecular weight are in progress.

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Correlation between crack growth rate and fracture mode transitions in low density polyethylene

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The fatigue crack propagation (*FCP*) behaviour of low density polyethylene (LDPE) has been described by Andrews and Walker[1] and by Hertzberg *et al.*[2]. The results published by the former authors showed a discontinuity in the *FCP* behaviour of this material at a crack growth rate of $\sim 10^{-3}$ mm/cycle; no such discontinuity in fatigue reponse was reported in the latter study. We have since re-examined the *FCP* behaviour at 10 Hz of compact-tension specimens of LDPE as a function of ΔK, over a wider range of ΔK (*Figure 1*). These data show a decrease in crack growth rates ($\mathrm{d}a/\mathrm{d}N$) with increasing ΔK between $\Delta K = 0.4$ MPa $\mathrm{m}^{1/2}$ and 0.6 MPa $\mathrm{m}^{1/2}$, followed by an increase in $\mathrm{d}a/\mathrm{d}N$ with ΔK above 0.6 MPa $\mathrm{m}^{1/2}$; the solid lines shown in *Figure 1* represent the data reported in ref 2. Thus the absence of any discontinuity in *FCP* behaviour for LDPE reported in the earlier study[2] can be traced to the fact that the entire ΔK test range was above the transition range identified in the present investigation.

Since Andrews and Walker evaluated *FCP* rates as a function of $\mathcal{T}$, an elastic-plastic surface work parameter, while Hertzberg *et al.* measured crack growth rates as a function of the elastic stress intensity factor range, ΔK, these results cannot be compared directly. Nevertheless, it is interesting to note that the crack growth rate corresponding to the transition at A ($\mathrm{d}a/\mathrm{d}N \sim 10^{-3}$ mm/cycle) agrees closely with the *FCP* rate at the discontinuity reported by Andrews and Walker[1]. Thus, a phenomenological similarity is apparent between the LDPE data reported by Andrews and Walker and the present results which must reflect an equivalent intensity of the stress–strain field at the advancing crack tip.

An examination of the fracture morphology of LDPE revealed a marked change in the fracture surface appearance at the $\mathrm{d}a/\mathrm{d}N$–ΔK transition at location B (*Figure 1*). Below $\Delta K = 0.6$ MPa $\mathrm{m}^{1/2}$, the fracture surface exhibited a tufted appearance consisting of small voids, while large voids dominated the fracture topography at higher ΔK levels (*Figures 2a* and *2b*). This contrast in appearance is striking, considering the difference in magnification between *Figures 2a* and *2b* ($\sim$700x and 20x,

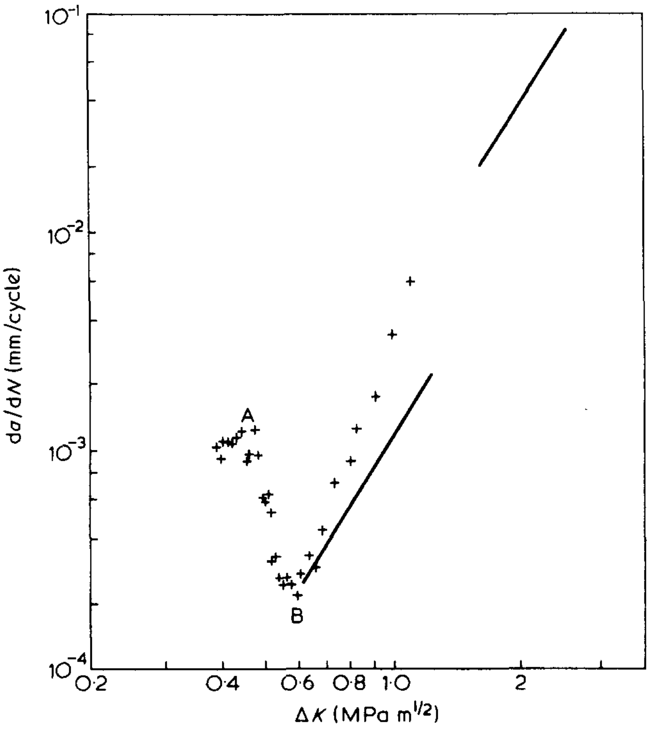

Figure 1 Fatigue crack growth rates at 10 Hz as a function of ΔK in LDPE. Note the decrease in $\mathrm{d}a/\mathrm{d}N$ with increasing ΔK between A and B. Solid lines represent *FCP* data for LDPE from ref 2

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