Sedimentation behaviour in dilute solutions of a polyelectrolyte

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Sedimentation velocity studies are reported for dilute aqueous solutions of sodium poly(styrene sulphonate) with various quantities of added NaCl. On increasing the salt concentration the dependence of 1/S on polymer concentration decreases and, up to 0.5 M NaCl, the limiting sedimentation coefficient increases. These changes are related to changes in the effective charge on the polymer, which increases with increasing salt concentration, and in the friction coefficient, which decreases with increasing salt concentration. The effective charge on the polymer should be considered when evaluating the Mandelkern–Flory parameter, $\phi^{1/3}P^{-1}$.

(Keywords: analytical ultracentrifuge; sedimentation velocity; sodium poly(styrene sulphonate); polyelectrolyte; charge effects)

INTRODUCTION

Polyelectrolytes are increasingly important in industry and there is a need for reliable ways of characterizing them in solution. Sedimentation velocity in the analytical ultracentrifuge can provide a useful insight into the size and shape of polymer molecules in solution. However, the sedimentation behaviour of polyelectrolytes is still poorly understood. In this paper, sedimentation in dilute solutions of sodium poly(styrene sulphonate) is described and discussed.

The presence of charged groups on a polymer influences its solution behaviour in a number of ways:

(1) Interactions between charged sites on the polymer affect the conformation of the polymer. In pure water the chain is expanded, on adding a salt the chain contracts.

(2) Charges on the polymer interact with small ions in the solution. If the polyelectrolyte has a high charge density, some counterions may condense on the surface, reducing the effective charge density to a critical value[1]. The remaining counterions are distributed in solution around the polyion forming an 'ionic atmosphere'. As a salt is added to the solution the thickness of the ionic atmosphere decreases.

(3) In transport experiments, such as sedimentation and diffusion, the rate of movement of the polyelectrolyte is affected by its charged nature. In pure water the sedimentation coefficient for the polyelectrolyte is lower, and the diffusion coefficient is higher, than for an equivalent uncharged polymer. This has been called the 'primary charge effect'[2] and has been attributed to the electric field set up if a charged macromolecule is separated from its counterions. The polyion and its counterions are forced to move together at a velocity intermediate between that which each would have alone. Addition of a salt reduces this primary charge effect, the sedimentation coefficient increases and the diffusion coefficient decreases.

It has been suggested[3] that the primary charge effect is virtually eliminated at infinite dilution of polyion in the presence of a salt. However, as has also been pointed out[4,5], the effect of charge on the distribution of small ions is not negligible under these conditions, and this will influence observed transport properties. This paper deals with the influence of charge effects on the sedimentation coefficient as the concentration of added salt is changed.

EXPERIMENTAL

Two samples of sodium poly(styrene sulphonate) were obtained from Polymer Laboratories Limited (Church Stretton, Shropshire, UK). Nominal molecular weights were given as 1×10^5 g mol^{-1} for Sample 1 and 7.8×10^5 g mol^{-1} for Sample 2 and $\bar{M}_w/\bar{M}_n$ was quoted as being less than 1.1. The weight-average molecular weight of Sample 1 was measured in this laboratory by low angle laser light scattering, using a Chromatix KMX-6 instrument, and was found to be 1.04×10^5 g mol^{-1}. The samples as received contained ca. 10% water. They were either dried to constant weight, in a vacuum oven at 70°C, before use or used as received, in which case concentrations were corrected to allow for the moisture content.

Sedimentation velocity experiments were carried out at 40 000 rev/min and 23°C using a Beckman Model E Analytical Ultracentrifuge equipped with a phaseplate Schlieren optical system. Sedimentation coefficients were calculated from the rate of movement of the maximum in the Schlieren image. The sedimentation behaviour was studied for several concentrations of polymer in distilled water with various quantities of added NaCl (Fisons, A.R. grade).

RESULTS

The experimental results are shown in *Figure 1*, which is a plot of the reciprocal of the observed sedimentation coefficient, $1/S$, against polymer concentration in g cm^{-3}, c. It can be seen that the dependence of $1/S$ on c decreases as the salt concentration increases. *Figure 2a* shows the variation with salt concentration of the limiting sedimentation coefficient, S^0, which increases with increase in NaCl concentration up to 0.5 M.

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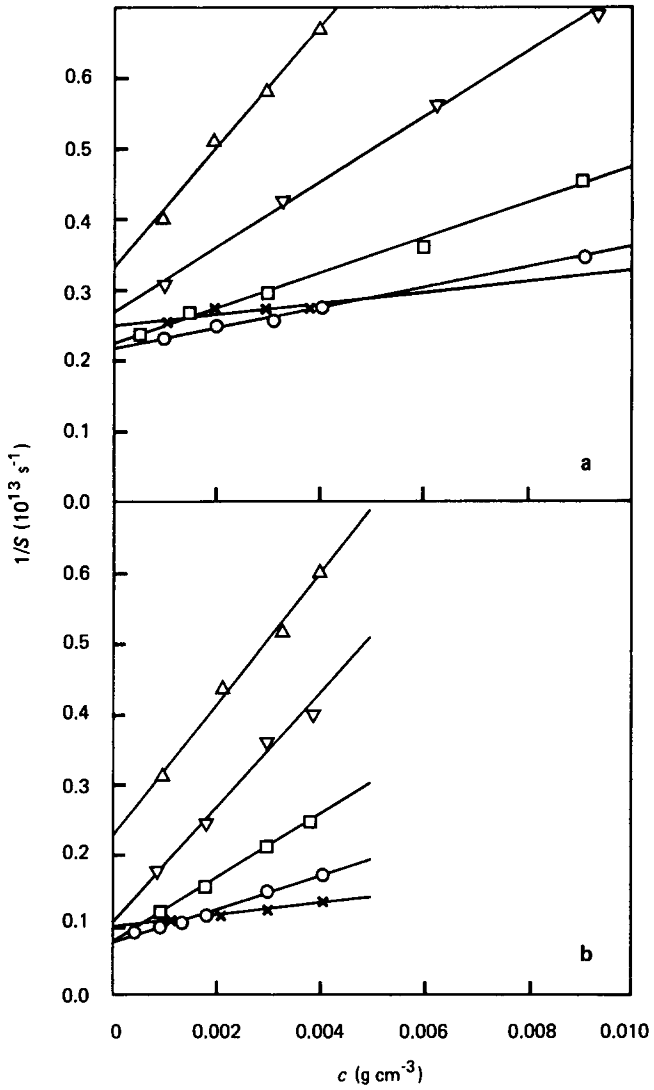

Figure 1 Dependence of reciprocal of observed sedimentation coefficient on polymer concentration for (a) Sample 1 and (b) Sample 2. NaCl concentrations are 0.005 M (△), 0.02 M (▽), 0.1 M (□), 0.5 M (○) and 2 M (×)

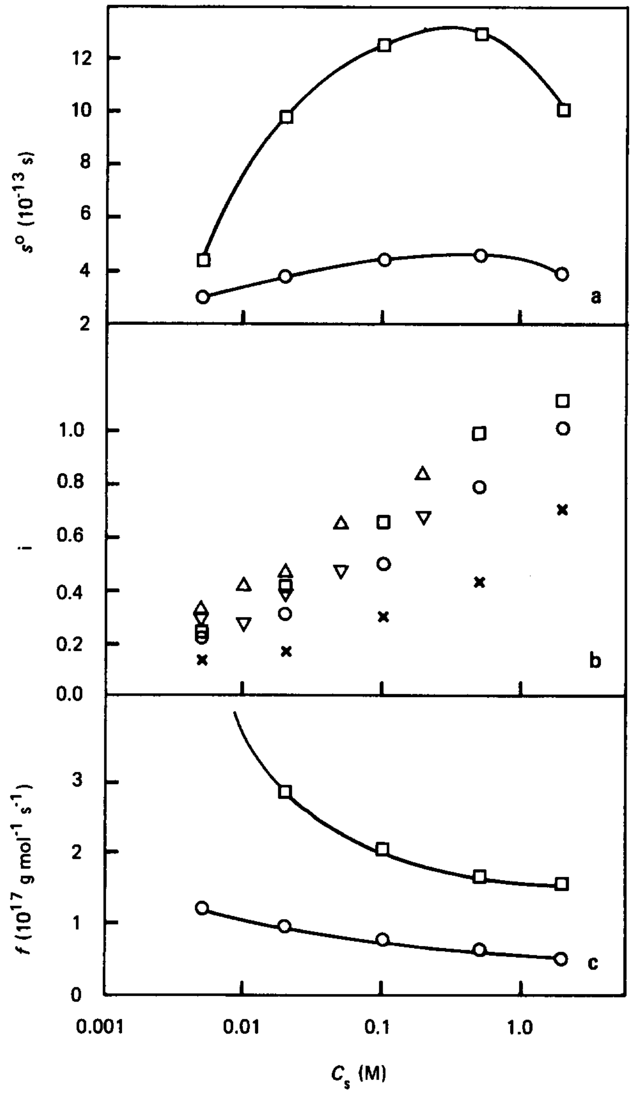

Figure 2 Dependence of (a) limiting sedimentation coefficient, (b) effective charge parameter and (c) molar friction coefficient on NaCl concentration for Samples 1 (○) and 2 (□). Plot (b) includes data for samples of $\bar{M}_w$ 3.9×10^5 (▽) and 2.34×10^6 (△) g mol^{-1} from ref. 4, and values calculated for Sample 1 assuming the non-ionic contribution to the slope of the $1/S$ vs. c plot to be given by $1.6[\eta]/S^0$ (×)

DISCUSSION

Theory

The classical treatment of sedimentation of polyelectrolytes[2,3,6] sees the actual velocity of the polyion as having two components: a contribution from the centrifugal field and a contribution from the internally created electric field. An alternative, more rigorous, treatment involves the application of irreversible thermodynamics[5,7]. Following a classical approach Eisenberg[6,8] obtains, for the sedimentation coefficient of a polyelectrolyte:

$$\frac{1}{S}=\frac{f}{\bar{M}-\frac{1}{2}iZ\bar{M}_s}+\frac{C_u i^2}{C_s(2\bar{M}_u-i\bar{M}_s)}\left\{f_s-\frac{\bar{M}_s f}{2\bar{M}-iZ\bar{M}_s}\right\} \quad (1)$$

Here f is the molar friction coefficient of the polyion and f_s the molar friction coefficient of the salt ions. If the co- and counterions have different mobilities a secondary charge effect arises which complicates the situation, but this is not a problem with NaCl. The parameter Z is the number of ionizable groups on the polymer; $C_u = CZ$ where C is the molar concentration of polyelectrolyte; C_s is the molar concentration of the salt; $\bar{M} = M(1-\bar{v}\rho)$, where M is the molecular weight of the polyelectrolyte, $\bar{v}$ its partial specific volume and ρ the density of the solution; $\bar{M}_u = M_u(1-\bar{v}\rho)$, where $M_u = M/Z$; $\bar{M}_s = M_s(1-\bar{v}_s\rho)$, where M_s is the molecular weight of the salt and $\bar{v}_s$ its partial specific volume.

The parameter i is an effective charge parameter, which takes account of interactions of the polyion with its counterions. On average $(1-i)Z$ counterions are assumed to interact in some way with the polyelectrolyte, so that it carries an effective charge of iZ. No assumptions are made regarding the nature of the interaction. One may expect that the effective charge on the polymer is determined both by the number of 'condensed' counterions and by the extent of atmospheric screening.

Equation (1) may be rearranged to give:

$$\frac{1}{S}=\frac{1}{S^0}(1+kc) \quad (2)$$

where c is the concentration of the polyelectrolyte component in g cm^{-3}, k is given by:

$$k=\frac{10^3Z^2i^2}{2C_sfM}\left\{f_s-\frac{\bar{M}_s}{2S^0}\right\}$$

and S^0, the limiting sedimentation coefficient, is given by:

$$S^0=\frac{\bar{M}-\frac{1}{2}iZ\bar{M}_s}{f} \qquad (3)$$

Equation (2) demonstrates that a plot of $1/S$ against c should be linear, as was observed. This equation describes the effect of charge alone on the sedimentation coefficient of a polyelectrolyte. The normal nonionic concentration dependence of S has not been considered, so this equation does not provide a complete picture of the sedimentation behaviour of polyelectrolytes. Nevertheless, it is informative to consider the implications of equation (2).

If i and f are both independent of salt concentration, the slope of a plot of $1/S$ against c should be proportional to $1/C_s$. Whilst such a relationship has been observed in a study of low molecular weight poly-L-lysine hydrohalides[9], in general, for a high molecular weight, high charge density, polyelectrolyte both i and f can be expected to vary with salt concentration. The present work confirms a previous observation[4] that there is not a linear relationship between the slope of a plot of $1/S$ against c and $1/C_s$ for sodium poly(styrene sulphonate).

Effective charge parameter

Using equation (2), it can be shown that:

$$ai^2+bi+c=0 \qquad (4)$$

where

$$a=\frac{10^3Z^2}{2C_sM\Delta}\left\{f_s-\frac{\bar{M}_s}{2S^0}\right\}$$

$$b=Z\bar{M}_s/2$$

$$c=-\bar{M}$$

and Δ is the slope of the $1/S$ against c plot. Values of i calculated using equation (4) are shown in *Figure 2b*. The Figure includes some values calculated from the results of Nagasawa and Eguchi[4]. In the calculations the partial specific volume, $\bar{v}$, for sodium poly(styrene sulphonate) was taken to be 0.6, f_s was taken as 3×10^{15} g mol^{-1} s^{-1} and $\bar{M}_s$ was taken as 40 g mol^{-1}.

It can be seen that i increases significantly with increasing salt concentration. The same trend has been observed for the effective charge exhibited by polyelectrolytes in experiments involving thermodynamic equilibrium[10,11]. The equilibrium effective charge parameter may be equated to twice the Donnan distribution parameter, Γ, but it is not clear whether or not this should be the same as i in a transport experiment. The theoretical limiting value of 2Γ, calculated using Manning's theory[12], is 0.18.

Friction coefficient

Once i has been determined, the molar friction coefficient can be calculated using equation (3). As can be seen in *Figure 2c*, f decreases with increasing salt concentration. The values of f shown are corrected to the viscosity of water. This is a complex friction coefficient and the observed change is probably due to two factors:

(1) a decrease in coil dimensions as the chain contracts and
(2) a decrease in the effect of the ionic atmosphere as the thickness of the ionic atmosphere decreases.

It is the dominant effect of the decrease in f which leads to S^0 increasing in the range of salt concentrations 0.005 to 0.5 M.

Non-ionic concentration dependence

As stated above, the equations used neglect the normal non-ionic concentration dependence of S. The experimental slope of the $1/S$ against c plot may be expected to be greater than that due to charge effects alone. Consequently, the true values of i will be lower, and those of f higher, than those calculated as above, but the trends observed are almost certainly real. The crosses in *Figure 2b* show the values of i calculated for Sample 1 if the non-ionic contribution to the slope of the $1/S$ against c plot is taken to be $1.6[\eta]/S^0$, a relationship frequently observed for non-ionic polymers in good solvents[13].

Mandelkern–Flory parameter

Sedimentation and viscosity data may be combined to yield a value for molecular weight, if the Mandelkern–Flory parameter, $\Phi^{1/3}P^{-1}$, is known. For non-ionic polymers $\Phi^{1/3}P^{-1}$ is given by[14]:

$$\Phi^{1/3}P^{-1}=\frac{S^0N_A\eta_0[\eta]^{1/3}}{M^{2/3}(1-\bar{v}\rho)} \qquad (5)$$

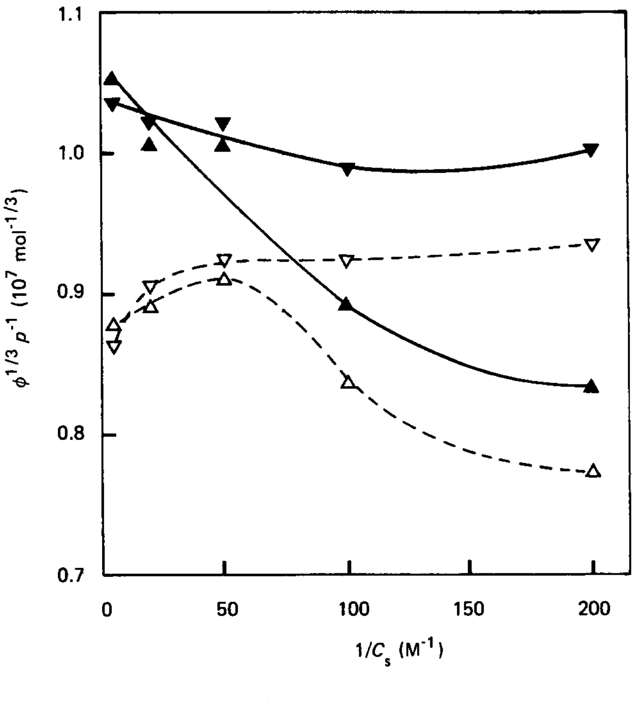

Figure 3 Dependence of $\Phi^{1/3}P^{-1}$ on reciprocal of NaCl concentration for samples 7 (△▲) and 9 (▽▼) of ref. 4, calculated according to equations 5 (open symbols, dashed lines) and 6 (filled symbols, solid lines)

where N_A is Avogadro's number; η_0 is the solvent viscosity and $[\eta]$ is the intrinsic viscosity of the polymer. For non-ionic polymers the value of $\Phi^{1/3}P^{-1}$ is generally close to 1.1×10^7 mol$^{-1/3}$ (2.5×10^6 if $[\eta]$ is expressed in dl g^{-1})[15]. For polyelectrolytes lower values have been found[4,16,17]. Equation (5) should be modified for the case of polyelectrolytes. Using equation (3) for the limiting sedimentation coefficient, the expression for $\Phi^{1/3}P^{-1}$ becomes:

$$\Phi^{1/3}P^{-1} = \frac{S^0 N_A \eta_0 [\eta]^{1/3}}{M^{2/3}\left\{(1-\bar{v}\rho) - \dfrac{iZ\bar{M}_s}{2M}\right\}} \tag{6}$$

If $i = 2\Gamma$, as discussed above, the expression given by Eisenberg[18] is obtained. Nagasawa and Eguchi[4], in their study of sodium poly(styrene sulphonate), calculated $\Phi^{1/3}P^{-1}$ by means of equation (5), and observed an anomalous decrease at high ionic strengths. Their results for two samples are shown in *Figure 3*. If $\Phi^{1/3}P^{-1}$ is recalculated using equation (6), as is also shown in *Figure 3*, the decrease at high ionic strengths is eliminated and the limiting value of $\Phi^{1/3}P^{-1}$ is closer to, though still lower than, the accepted value for non-ionic polymers.

CONCLUSIONS

There is no simple extrapolation which allows all effects of charge on the sedimentation behaviour of a polyelectrolyte to be ignored. At any salt concentration, the result of extrapolating to zero polymer concentration is affected by:

(1) the effective charge on the polymer and
(2) the influence of the ionic atmosphere and of the polymer conformation on the friction coefficient.

At low salt concentrations, i is small but large effects of charge on f can be expected. At higher salt concentrations, effects on f are smaller, but i is larger. The variation of the effective charge parameter with salt concentration should be taken into account if sedimentation data are to be combined with viscosity data by means of the Mandelkern–Flory relationship.

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