

# The dielectric increments of aqueous polyelectrolyte solutions: a scaling approach<sup>☆</sup>

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## Abstract

This paper deals with dielectric dispersion curves (covering a frequency range from a few Hz to 100 MHz) of Na – poly(styrene-sulfonate) of  $65\,000 \leq M_w \leq 1\,060\,000 \text{ g mol}^{-1}$  in aqueous solutions. The values of the low frequency ( $\Delta \in_1$ ) and high frequency ( $\Delta \in_2$ ) dielectric increments, obtained from the experimental curves matched to a superposition of two Cole–Cole equations, have been analyzed in terms of their concentration and molar mass dependence. The concentrations  $C \text{ (g l}^{-1}\text{)}$  of the various solutions were mostly situated in the transition regime defined by Odijk [T. Odijk, *Macromolecules* 12 (1979) 688] between the dilute regime ( $C < C_g^*$ ) and the semi-dilute one ( $C > C^{**}$ ), and wherein the characteristic concentration  $C^*$  marks the onset of flexibility effects on the polyion behavior. It has been shown that in the concentration range  $C_g^* < C < C^{**}$  the increments in both frequency domains satisfy a scaling relation  $\Delta \in_j = B_j M^{v_j} (C/C^*)^{\mu_j}$  with molar mass independent exponents  $v_j$  and  $\mu_j$  changing around  $C^*$ . Their values are different for  $\Delta \in_1$  and  $\Delta \in_2$ , except for  $\mu$  above  $C^*$  where both increments appear to become concentration-independent. Below  $C_g^*$ , in the dilute regime, the two dispersion domains seem to merge. The increment  $\Delta \in = \in' (0) - \in (\infty)$  is molar mass independent if scaled to  $(C/C_g^*)$ . The molar mass dependence of the increments as a function of the macromolecular concentration  $\rho_p$ ,  $\Delta \in$  or  $\Delta \in_j \sim M^\gamma (\rho_p)^\mu$ , also reveals differences between the different concentration regimes. Extrapolation from above  $C_g^*$  to zero concentration is thus unjustified. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Polyelectrolytes; Dielectric dispersion; Dielectric increments; Scaling relations; Na-poly(styrene-sulfonate); Concentration regimes

<sup>☆</sup>The experimental data presented in this paper have been measured by F.J.M. Pleyte with the help of J.P.M. van der Ploeg both working in this laboratory

## 1. Introduction

The dielectric behavior of aqueous polyelectrolyte solutions is one of the peculiar properties of these systems. In particular the relative permittivities of strong polyelectrolytes in pure aqueous solutions are noticeably large at very low frequencies if compared to those of uncharged macromolecules or low molar mass electrolyte solutions. In general two distinct dispersion regions extending up to approximately 100 MHz are found (1).

There is still no good and fully consistent theory available for the dielectric properties of aqueous polyelectrolyte solutions. Most theoretical approaches neglect the interaction between polyions and the influence of the polyions on the solvent, whether they start from naive models (2) or try to derive the dielectric properties of such solutions from a more rigorous theory of the complex conductivity in a frequency-dependent electric field. Several such theories have been proposed for solutions of spherical or rigid rodlike macromolecules (or colloidal particles). They all practically deal with solutions at infinite dilution and in the presence of an excess of added salt (3–11). Most polyelectrolyte solutions that have been investigated do not satisfy these conditions. Moreover, none of these theories predicts the two dispersion regions which have been observed with most aqueous polyelectrolyte solutions.

The complex conductivity approach is the analogue of the Debye–Falkenhagen theory (12) for strong low molar mass electrolytes which predicts dielectric increments  $\Delta\epsilon$  minute compared to those of polyelectrolyte solutions. Furthermore, it has been shown that the Debye–Falkenhagen effect is not the only one responsible for the dielectric response of electrolyte solutions. Others become operative at the lowest concentrations leading to dielectric decrements. They include, with increasing concentration, the kinetic depolarization effect (13,14) and the dielectric saturation (15,16). Both involve the influence of the small ions on the polarization of the solvent. All three effects have been observed experimentally (17–21), although there are some quantitative discrepancies between several authors due to ex-

perimental difficulties. The theory of each of the three effects has been treated independently and not together in an unified theory as is preferable.

New theoretical developments are badly needed to understand the dielectric properties of aqueous polyelectrolyte solutions, particularly the frequency dependence of the relative permittivity,  $\epsilon'$ , and the influence of polyion size and concentration. This is by no means a simple task; in the absence of an excess low molar mass electrolyte concentration spherically symmetrical conditions around the polyion are not valid (except perhaps at the highest concentrations) and concentration effects are complicated. For dielectric behavior this may be even more serious than for other polyelectrolyte properties as many specific effects will have to be taken into account.

To stimulate such developments extensive and systematic experimental results may be a helpful tool particularly if not limited in the frequency and concentration range. In recent years only few of such studies have been published, mainly focussed on the high frequency dielectric properties of sodium polystyrene sulfonate (NaPSS) (22,23).

In the next section some succinct details concerning recent measurements from this laboratory will be presented. This will be followed in Sections 3 and 4 by a critical analysis and, finally, in Section 5 some provisional conclusions will be drawn.

## 2. Some experimental details

The electric properties of seven molar masses,  $M_w$  of 65 000, 88 000, 177 000, 354 000, 690 000, 780 000 and 1 070 000 g mol<sup>-1</sup>, respectively of the strong polyelectrolyte Na-poly(styrene sulfonate) NaPSS (Pressure Chemical Co. and Polymer Laboratories) have been investigated. The samples are of low polydispersity, fully dissociated in aqueous solutions and bear one charged group on each monomeric unit. They have been studied recently in this laboratory using low amplitude electric fields extending in frequency from a few hertz to 100 MHz (Pleyte et al., unpublished results). The electric properties of the various NaPSS samples dissolved in deionized water (con-

ductivity always lower than  $10^{-6}$  S cm $^{-1}$ ) and dialyzed against pure water for several days to remove low molar mass contaminants, have been measured as a function of frequency and concentration, mainly in the absence of added salt.

The concentrations  $C$  ranged from a few hundred to several grams per liter. The upper concentration range was limited by the conductivity of the solutions, the lower one by the increasingly perturbing fluctuations in  $\epsilon'$  with decreasing concentrations due to the drift in the conductance of the solutions.

All concentrations explored (except the lowest concentrations of the three lowest molar masses) are larger than the critical concentrations  $C_g^*$  as defined by de Gennes et al. (24), below which highly charged polyions are assumed to be rodlike and to rotate freely. They are in the transition concentration regime which encloses the critical concentration  $C^*$  around which the flexibility of the chain starts to play a role according to Odijk (25). This regime, where interactions between polyions cannot be neglected, is also characterized by an upper critical concentration,  $C^{**}$  where the true semi-dilute regime is assumed to start (26). Concentrations close to  $C^{**}$  could not be investigated.

Two different measuring devices have been used to measure the complex permittivities of the polyelectrolyte solutions. In the low frequency range (from a few Hz to 10 kHz) where large electrode polarization effects are a considerably perturbing factor, a relative permittivity meter for electrically conducting solutions developed and constructed in this laboratory (27) has been used (equipment A). The lowest frequency attainable depends on the R-C product of the solution. Although equipment A theoretically eliminates the effects of electrode polarization, in practice a small residual electrode polarization effect persists. In the determination of the relative permittivity of the polyelectrolyte solutions this has been taken care of in an empirical way by making the measurements of each sample solution with respect to a reference solution (e.g. sodium benzoate) of the same conductivity (27). For most solutions investigated the measured relative

permittivities  $\epsilon'$  thus corrected reach, at the lowest frequencies investigated, a constant value within a few units. The error on the relative permittivity with equipment A has been discussed in detail in the previous publication (27). At the lowest frequency the accuracy is estimated to be better than a few percent or 2–3 units, whichever is the larger, but it increases somewhat with increasing frequency.

In the frequency range 2.5 kHz to 100 MHz a Hewlett-Packard LF Impedance/Gain phase analyzer (model # 4194 A), equipment B, calibrated according to the manufacturer's recommendations. Two measuring cells have been utilized. From 2.5 kHz to 10 MHz, where electrode polarization may not have disappeared completely, a cylindrical cell with plane, parallel platina electrodes of variable spacing was used (28,29). For the range 1–100 MHz a coaxial type cylindrical condenser of variable liquid height (30) was available. The theoretical precision on  $\epsilon'$  with equipment B largely depends on the frequency and the conductivity of the sample but is always equal to or smaller than 3%. In practice the values of  $\epsilon'$  will be accurate to one or two units.

There is some overlap in the measuring range of equipment A and B, and in the range of the two cells used with B. The data obtained in two different ways coincided satisfactorily within the estimated experimental error.

All measurements have been performed at constant temperature ( $21.00 \pm 0.05^\circ\text{C}$ ).

### 3. Analysis of the dielectric dispersion curves

At a constant concentration analogous dispersion curves ( $\epsilon'$  as a function of the frequency) have been observed for all aqueous NaPSS solutions, also in agreement with what has been found previously (1). In most cases two separate parts can be distinguished: a low-frequency dispersion region extending to approximately 100 kHz and a second, high-frequency one which covers the remaining frequency region up to 100 MHz, where the value of  $\epsilon'$  for pure water is reached. The two dispersions may overlap in a certain fre-

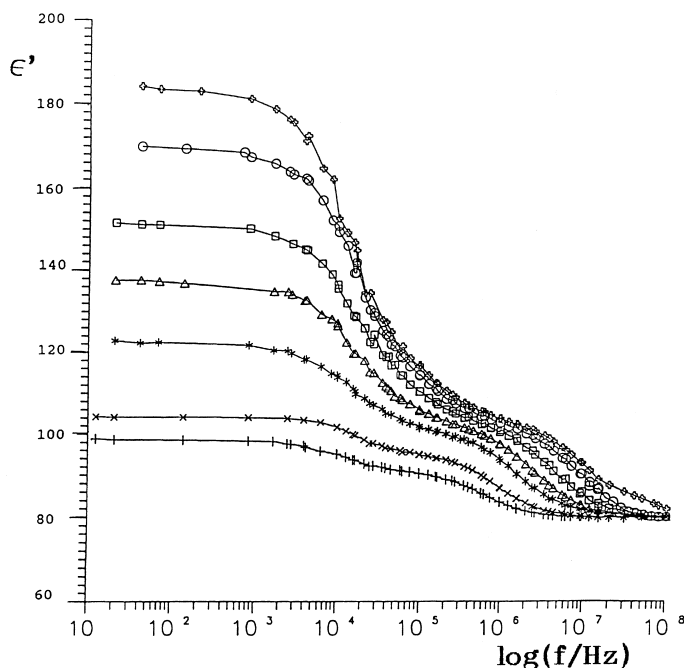


Fig. 1. Relative permittivity  $\epsilon'$  vs. frequency of NaPSS ( $M = 177\,000$ ) at various concentrations: ( $C/g\ l^{-1}$ ) = 0.044 (+), 0.090 (x), 0.235 (\*), 0.450 ( $\Delta$ ), 0.690 ( $\square$ ), 1.380 ( $\circ$ ) and 1.800 ( $\diamond$ ). The drawn curve is the fitted double Cole–Cole Eqs. (1a) and (1b).

quency range but generally the two regions can be distinguished by visual inspection (Figs. 1–3). Moreover, they differ significantly in their dependence on the molar mass. In the low-frequency domain the amplitude of the dispersion, at comparable concentrations, increases considerably with the molar mass  $M$  of the polyelectrolyte. In the high-frequency end this amplitude seems to depend only very weakly on  $M$  if at all, as will be discussed in more detail hereafter. For a quantitative discussion of the dispersion curves it is useful to represent them by an analytical expression. As no reliable theoretical equation is available an empirical approach is necessary. The experimental dispersion curves have been fitted by a non-linear least squares procedure to a superposition of two Cole–Cole dispersion equations for the real part of the complex relative permittivity (31)

$$\epsilon'(\omega) = \epsilon_{\infty} + \Delta \epsilon_1 g_1(\bar{\tau}_1, \beta_1) + \Delta \epsilon_2 g_2(\bar{\tau}_2, \beta_2) \quad (1a)$$

$$g_j(\tau_j, \beta_j) = \frac{1 + (\omega \bar{\tau}_j)^{\beta_j} \cos(\beta_j \pi / 2)}{\left[ 1 + (\omega \bar{\tau}_j)^{2\beta_j} + 2(\omega \bar{\tau}_j)^{\beta_j} \cos(\beta_j \pi / 2) \right]} \quad (1b)$$

where  $\omega = 2\pi f$  is the circular frequency,  $\epsilon_{\infty}$  the high-frequency limit of the relative permittivity;  $\Delta \epsilon_1$  and  $\Delta \epsilon_2$  are the amplitudes of the low- and the high-frequency dispersion, respectively,  $\bar{\tau}_1$  and  $\bar{\tau}_2$  their mean relaxation times,  $\beta_1$  and  $\beta_2$  their respective Cole–Cole parameters. These parameters  $0 \leq \beta_i \leq 1$  take into account the deviations of the Cole–Cole curve from a Debye relaxation ( $\beta = 1$ ). The Cole–Cole expression corresponds to a dispersion curve with a distribution of relaxation times, the extent of which is measured by the parameter  $\beta$ ; the more  $\beta$  departs from unity the larger the distribution. The relaxation time in this expression is the mean value of the relaxation times in the distribution. The single Cole–Cole curve is centrosymmetric with respect to the point  $\omega = 1/\bar{\tau}$  where the amplitude reaches half its total value.

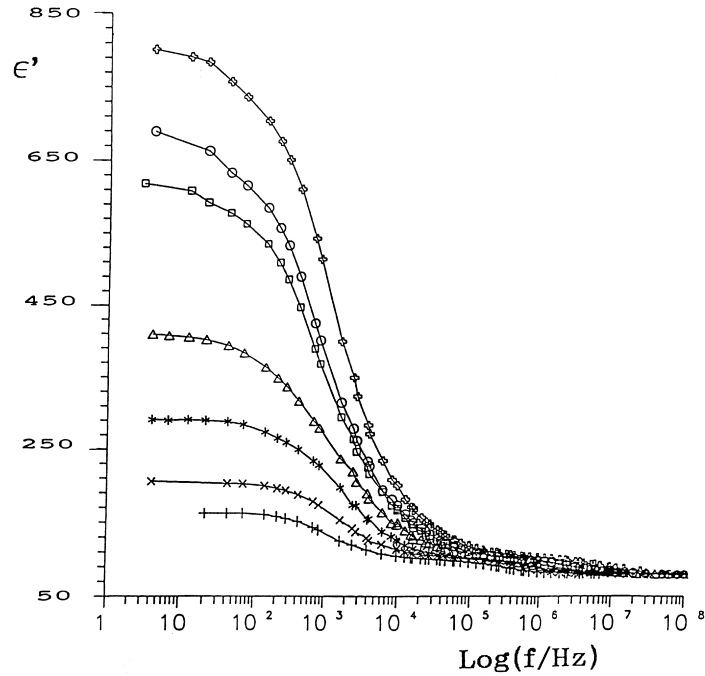


Fig. 2. Relative permittivity  $\epsilon'$  vs. frequency of NaPSS ( $M = 354\,000$ ) at various concentrations:  $C/\text{g l}^{-1} = 0.032$  (+),  $0.064$  (x),  $0.1275$  (\*),  $0.250$  ( $\Delta$ ),  $0.510$  ( $\square$ ),  $0.630$  ( $\circ$ ) and  $1.275$  ( $\diamond$ ). The drawn curve is the fitted double Cole–Cole Eqs. (1a) and (1b).

The possibility of matching an experimental dispersion curve to the Cole–Cole equation does not imply that the former has these same characteristics. The flexibility of the Cole–Cole expression due to the combination of  $\bar{\tau}$  and  $\beta$  makes it possible to fit dispersion curves that do not have such properties. A striking example is the rather excellent fit of the Debye–Falkenhagen dispersion curve for the electric increment of an electrolyte solution (11) to the single Cole–Cole expression with the same  $\epsilon'(0) = \epsilon'(\omega \rightarrow 0)$  and  $\epsilon'_\infty$  (Fig. 4). The former has, however, a very complicated frequency dependence with a single relaxation time  $\tau_{\text{DF}}$ , and is clearly not centrosymmetric with respect to the point  $\omega = 1/\tau_{\text{DF}}$ .

$$x = \omega \tau_{\text{DF}}$$

$$\epsilon'(\omega) - \epsilon_s = [\epsilon'(0) - \epsilon_s]h(x)$$

$$h(x) = 2(1 + b^2) \left[ \frac{(Q/X)(b^2 - 1) + (R - b)}{(1 - b^2)^2 + x^2} \right] \quad (2)$$

$$Q = \left( \frac{[(1 + x^2)^{1/2} - 1]}{2} \right)^{1/2}$$

$$R = \left( \frac{[(1 + x^2)^{1/2} + 1]}{2} \right)^{1/2}$$

Here  $\epsilon'(\omega)$  is the relative permittivity of the electrolyte solution at frequency  $\omega$ ,  $\epsilon_s$  is the relative permittivity of the solvent and  $b$  is a quantity which depends on the valencies and the mobilities of the two species of ions in which the strong electrolyte dissociates. The frequency-dependent function  $h(\omega \tau_{\text{DF}})$  (with  $1 \geq h(x) \geq 0$ ) is larger than 0.5 for  $x = 1$ , its value depending on  $b$ . As a consequence the mean relaxation time  $\bar{\tau}$  obtained by the fit of the Debye–Falkenhagen relaxation curve to the Cole–Cole function does not equal  $\tau_{\text{DF}}$ . In the example of Fig. 4 the  $\tau_{\text{DF}} = 3.129 \times 10^{-10}$  s whereas from the fit the Cole–Cole mean relaxation time  $\bar{\tau} = 1.1 \times 10^{-10}$  s. Both relaxation times are of the same order of

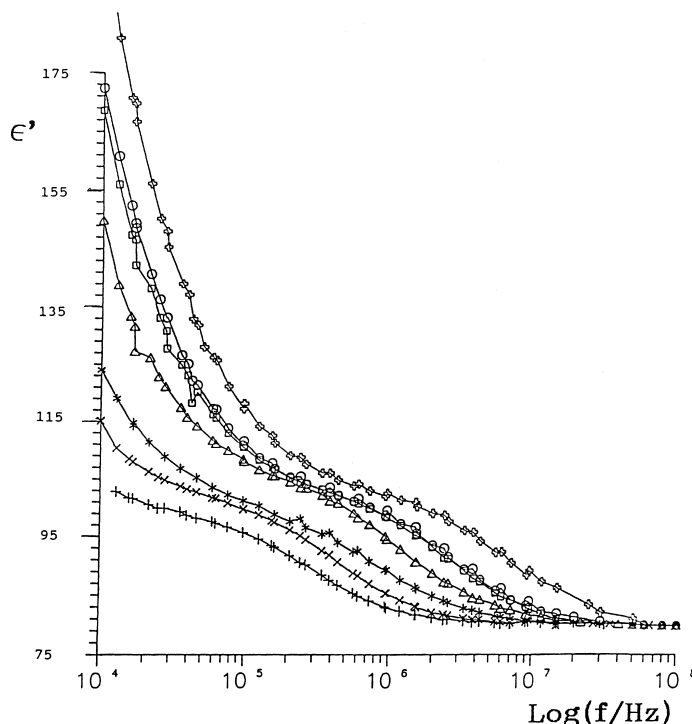


Fig. 3. Same solution as in Fig. 2 but at the higher frequency end ( $f > 10^4$ ) only with an expanded y-scale to demonstrate the existence of the high frequency dispersion region. The drawn curve is the fitted double Cole–Cole Eqs. (1a) and (1b).

magnitude but differ by approximately a factor of 3.

Other semiempirical dielectric relaxation equations besides the Cole–Cole expressions could be used as well such as, e.g. the Havriliak–Negami equation (32,33) which is not centrosymmetric but contains more adjustable parameters than the Cole–Cole equation. It does not yield significantly better fits and also remains an empirical expedient.

Eqs. (1a) and (1b) involve, for each system, in principle, *seven* adjustable fit-parameters. The Cole–Cole parameters,  $\beta_j$  are found to fluctuate unsystematically for all the curves analyzed,  $\beta_2$  being mostly close to unity (average  $\beta_2 = 0.9 \pm 0.04$ ). In contrast  $\beta_1$  is generally much smaller with an average of  $0.67 \pm 0.07$ . This could be an indication that the dispersion equation differs in the two frequency regions.

For all dispersion curves the fitted value  $\epsilon_\infty$  (average  $80 \pm 1$ ) was within experimental accu-

racy equal to the relative permittivity of water at the temperature of the measurements,  $\epsilon_s = 79.9$ . Thus the total amplitude  $\Delta\epsilon = (\epsilon(0) - \epsilon_\infty)$  of each dispersion curve is rather well established as  $\epsilon(0)$  coincides with the constant value of the measured permittivities at very low frequencies.

Of the six remaining adjustable parameters not too much significance can be given to the two relaxation times obtained by these fits as the  $\beta$ -values definitely deviate from unity. As indicated above they only are meaningful in as far as the order of magnitude of the physically relevant relaxation times is concerned. Also no clear interpretation of  $\beta_1$  and  $\beta_2$  can be given.

Notwithstanding reservations about the values of  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$ , as their values may somewhat depend on the fit procedure, we shall use them instead of  $\Delta\epsilon$  and  $\Delta\epsilon_2$  to obtain information from the dielectric dispersion curves of the polyelectrolyte solutions. We deem this is justified by the fact that the two dispersion regions are

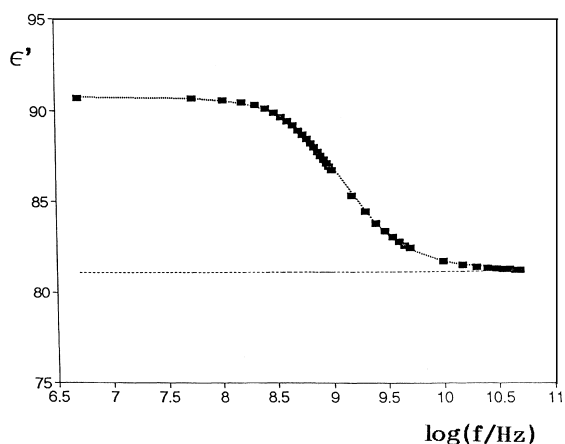


Fig. 4. The points represent the values of the Debye–Falkenhagen Eq. (2) for 0.1 M  $\text{MgSO}_4$  in water at 18°C, the dotted curve is the Cole–Cole fit for the same ( $\epsilon(\omega) - \epsilon_\infty$ ).

probably determined by different mechanisms, which will also become evident through their molar mass and concentration dependences. For  $M \geq 354\,000 \text{ g mol}^{-1}$  the deviation of ( $\Delta \epsilon_1 / \Delta \epsilon$ ) from unity is very small anyhow.

In the absence of good theoretical guidance some clarity in the experimental results of the various Na-PSS samples will be sought by an empirical scaling approach. Various concentration regimes will be considered according to the theoretical scaling expressions derived by Odijk for polyelectrolyte solutions without added salt (25,26).

$$C_g^* \approx \frac{M}{1000 N_{\text{Av}} L^3} \quad (3a)$$

$$C^* \approx \frac{M_m}{16\,000 \pi A Q N_{\text{Av}} L} \quad (3b)$$

$$C^{**} \approx \frac{M_m}{32\,000 \pi^2 A Q^2 N_{\text{Av}}} \quad (3c)$$

Here  $M$  and  $M_m$  are the molar mass of the polyelectrolyte and monomeric unit respectively,  $L = A(M/M_m)$  the polyelectrolyte contour length,  $N_{\text{Av}}$  the Avogadro constant,  $A$  the contour length per unit charge and  $Q = q^2/4\pi\epsilon_s\epsilon_o k_B T$  the

Bjerrum length (with  $q$  the elementary charge,  $\epsilon_o$  the absolute permittivity of vacuum,  $k_B$  the Boltzmann constant and  $T$  the temperature in Kelvin). Note that according to Eq. (8c) the critical concentration  $C^{**}$  is molar mass-independent.

To estimate these characteristic concentrations the value  $A = 0.17 \text{ nm}$  has been used which is the length of the projection of the monomeric unit on the axis of the polyion according to recent neutron scattering measurements (34). This assumes that every monomeric unit bears an elementary charge.

#### 4. The dielectric increment $\Delta \epsilon_1$ above $C_g^*$

As most of the concentrations investigated are in the range  $C_g^* \leq C (\text{g l}^{-1}) \leq C^{**}$  the concentrations will be scaled with respect to  $C^*$ . We presume the dielectric increments in that concentration range to satisfy the scaling relation

$$\Delta \epsilon_j = B_j M^{v_j} \left( \frac{C}{C^*} \right)^{\mu_j} \quad j = 1, 2 \quad (4)$$

with the constant  $B_j$  as well as the exponents  $\mu_j$  and  $v_j$  independent of  $M$  and  $C$ . Thus, at constant  $M$  this can be verified by plotting  $\log(\Delta \epsilon_j)$  against  $\log(C/C^*)$ .

$$\log(\Delta \epsilon_j) = V_j + \mu_j \log(C/C^*)$$

$$V_j = \log(B_j M^{v_j}) \quad (5)$$

In Figs. 5 and 6 the dielectric increments have been represented in this way. The lowest molar mass ( $M = 65\,000 \text{ g mol}^{-1}$ ) has been excluded in this figure because a majority of the concentrations are below or close to  $C_g^*$ . For the four and three lowest concentrations of the two higher molar masses this is also the case. They will be considered separately in Section 5. The concentration-dependence of  $\Delta \epsilon_1$  is considerable for  $C/C^* < 2.5$  (low concentrations or region a) but less for  $\Delta \epsilon_2$ . For both dispersion regions it is weak for higher values of  $C/C^*$  (high concentrations or region b).

For each molar mass  $\log(\Delta \epsilon_j)$  depends lin-

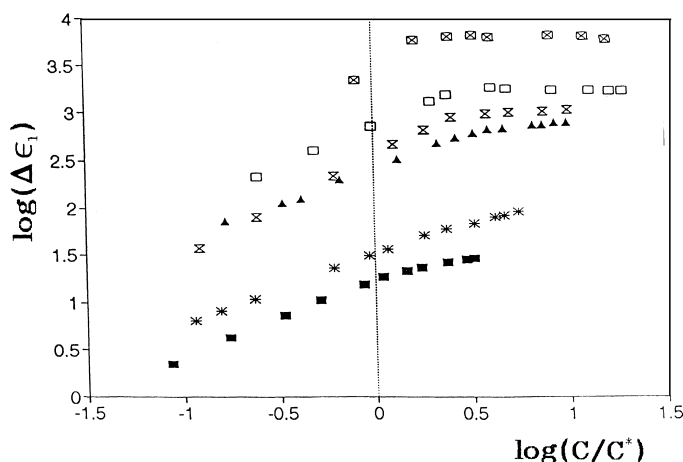


Fig. 5.  $\log(\Delta \epsilon_1)$  vs.  $\log(C/C^*)$  for different NaPSS molar masses (only concentrations of  $C > C_g^*$ ):  $10^{-3} \text{ M/g mol}^{-1} = 88$  (■), 177 (\*), 354 (Δ), 690 (x), 780 (□) and 1060 (⊠).

early on  $\log(C/C^*)$  indeed with different constants  $V$  and  $\mu$  in the low (a) and the high (b) concentration range. Two examples of  $\Delta \epsilon_1$  are shown in Fig. 7.

In Table 1 the values of the parameters  $V_{1,a}$  and  $V_{1,b}$  as obtained by a linear least squares fit together with the corresponding values for the high frequency dispersion  $V_{2,a}$  and  $V_{2,b}$  are collected for all samples but the lowest molar mass.

Where no data are presented not enough concentrations have been available to allow a fit; in all other cases the number of concentrations was just sufficiently large to allow a reliable least squares procedure.

The values of  $V_a$  and  $V_b$  definitely increase with molar mass for  $\Delta \epsilon_1$  but seem to decrease for  $\Delta \epsilon_2$ , although in the latter case the variations are small. One must, however, realize that

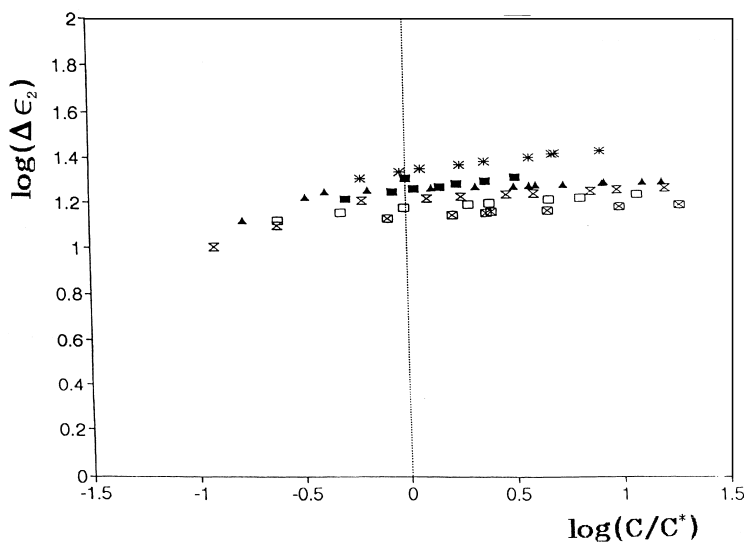


Fig. 6.  $\log(\Delta \epsilon_2)$  vs.  $\log(C/C^*)$  for different NaPSS molar masses (concentrations  $C > C_g^*$ ):  $10^{-3} \text{ (M/g mol}^{-1}) = 88$  (■), 177 (\*), 354 (Δ), 690 (x), 780 (□) and 1060 (⊠).



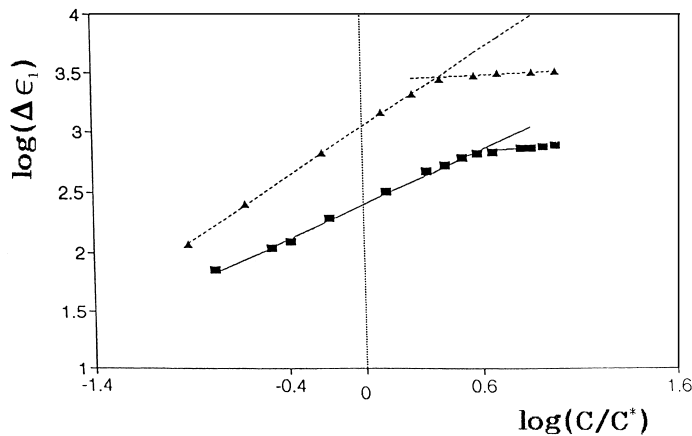


Fig. 7.  $\log(\Delta \epsilon_1)$  vs.  $\log(C/C^*)$  for  $M/\text{g mol}^{-1} = 354\,000$  (■) and  $690\,000$  (Δ); the straight lines are linear least squares fits.

the determination of a rather small value of  $\Delta \epsilon_2$  from a dispersion curve with a much larger value of  $\Delta \epsilon_1$  may be rather inaccurate, the more so as an empirical analytical expression has been fitted to the experimental points.

The values of the slopes  $\mu_{1,a}$  and  $\mu_{1,b}$  fluctuate around an average value, which are  $0.79 \pm 0.17$  and  $0.09 \pm 0.16$ , respectively, suggesting that for the high concentration region the slope might be zero.

It is possible to make almost all the curves in both Figs. 5 and 6 coincide by shifting them along the y-axis. These shifts ( $V_r - V$ ) dissimilar in the low frequency dispersion region for the two concentration regimes separated by  $\log(C/C^*) = 0.4$  but are identical in the high frequency one. They are determined with respect to an arbitrary reference molar mass  $M_r$  and follow directly from the scaling relation (4) at constant  $(C/C^*)$ .

$$\Delta \epsilon_j \left( \frac{M_r}{M} \right)^{v_j} = \Delta \epsilon_{j,r} \quad (6a)$$

$$\log(\Delta \epsilon_j) + S = \log(\Delta \epsilon_{j,r}) \quad (6b)$$

$$S = v_j \log \left( \frac{M_r}{M} \right) \quad (6c)$$

The reference molar mass was  $780\,000$  and  $354\,000 \text{ g mol}^{-1}$  for  $\Delta \epsilon_{1,a}$  and  $(\Delta \epsilon_{1,b})$ , respec-

tively, and  $690\,000 \text{ g mol}^{-1}$  for  $\Delta \epsilon_{2,a}$  and  $(\Delta \epsilon_{2,b})$ . A satisfactory single line vs.  $\log(C/C^*)$  is obtained for concentrations  $a$  as well as for  $b$  in the two dispersion regions (see as an example Fig. 8). A more precise concentration dependence can thus be determined than with each sample individually. A linear least squares fit to  $\log(C/C^*)$  of all  $\log(\Delta \epsilon_1) + S$  values for each set  $j, u$  results in the following equations.

$$\begin{aligned} \log(\Delta \epsilon_1) + S &= (2.86 \pm 0.01) \\ &+ (0.815 \pm 0.025) \log(C/C^*) \\ &\times C/C^* < 2.5 \end{aligned}$$

$$\begin{aligned} \log(\Delta \epsilon_1) + S &= (2.80 \pm 0.03) \\ &+ (0.04 \pm 0.04) \log(C/C^*) \\ &\times C/C^* > 2.5 \end{aligned}$$

$$\begin{aligned} \log(\Delta \epsilon_2) + S &= (1.179 \pm 0.009) \\ &+ (0.18 \pm 0.02) \log(C/C^*) \\ &\times C/C^* < 2.5 \end{aligned}$$

$$\begin{aligned} \log(\Delta \epsilon_2) + S &= (1.25 \pm 0.02) \\ &+ (0.02 \pm 0.02) \log(C/C^*) \\ &\times C/C^* > 2.5 \end{aligned}$$

For the lower concentration range the expo-

Table 1

Fit-parameters  $V$  for the low- and high-frequency dispersion [see Eqs. (4) and (5)]

Molar mass (g mol <sup>-1</sup> )	$V_{1,a}$	$V_{1,b}$	$V_{2,a}$	$V_{2,b}$
88 000	1.21 (0 ± 0.01)	–	1.245 (± 0.001)	–
177 000	1.505 (± 0.003)	1.810 (± 0.001)	1.31 (± 0.01)	1.33 (± 0.01)
354 000	2.39 (± 0.02)	2.75 (± 0.05)	1.25 (± 0.02)	1.252 (± 0.001)
690 000	2.542 (± 0.009)	2.93 (± 0.02)	1.18 (± 0.02)	1.20 (± 0.003)
780 000	2.854 (± 0.002)	3.244 (± 0.003)	1.2 (± 0.5)	1.162 (± 0.003)
1 060 000	–	3.82 (± 0.07)	–	1.122 (± 0.004)

nent of the concentration power law is significant but smaller than unity. In the higher concentration range  $\Delta \in_1$  and  $\Delta \in_2$  are practically concentration-independent, indeed, at least in the interval  $0.7 \geq \log(C/C^*) \geq 1.0$ . This is confirmed by the average values of  $\log(\Delta \in_{1,b}) + S$  and  $\log(\Delta \in_{2,b}) + S$  which are  $2.83 \pm 0.04$  and  $1.26 \pm 0.07$ , respectively.

A linear least squares fit of  $V_j$  to  $\log M$  (g mol<sup>-1</sup>) produces the values of  $\mu_{j,u}$

$$V_{j,u} = (V_o)_{j,u} + (v)_{j,u} \log M(\text{g mol}^{-1})$$

$$j = 1, 2 \quad u = a, b \quad (7)$$

$$V_{1,a} = -(7.3 \pm 1.6) + (1.7 \pm 0.2) \log$$

$$\times M(\text{g mol}^{-1})$$

$$V_{1,b} = -(10.1 \pm 2.8) + (2.3 \pm 0.4) \log$$

$$\times M(\text{g mol}^{-1})$$

$$V_{2,a} = V_{2,b} = (0.9 \pm 0.3)$$

$$- (0.12 \pm 0.05) \log M(\text{g mol}^{-1})$$

The actual molar mass dependence of  $\Delta \in_j$  must, however, be calculated with respect to the molecular concentration of the polyions,  $\rho_p = (C/M)N_{\text{Av}}$  and taking into account that also  $C^*$  depends on  $M$ .

$$\log(\Delta \in_{j,u}) = V_{j,u}^o - \mu_{j,u} \log(C^*)$$

$$+ \mu_{j,u} \log\left(\frac{M}{N_{\text{Av}}}\right) + \mu_{j,u} \log(\rho_p) \quad (8a)$$

$$= Z + (v_{j,u} + 2\mu_{j,u}) \log(M) + \mu_{j,u} \log(\rho_p) \quad (8b)$$

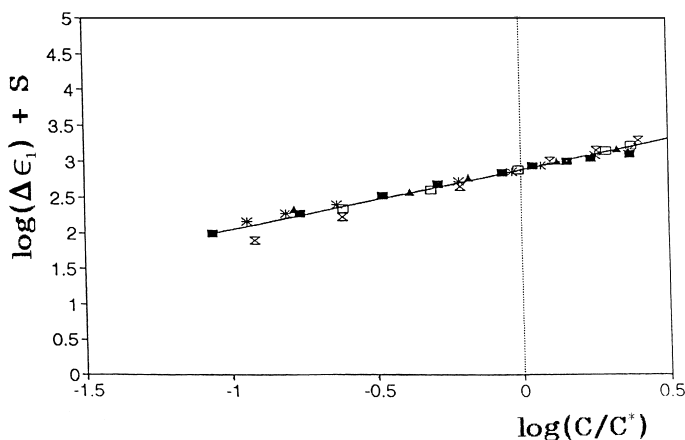


Fig. 8. The curves of Fig. 5 shifted along the y-axis to have them coincide with the curve for  $M/\text{g mol}^{-1} = 780\,000$  in the concentration region  $C < 2.5 C^*$ . The drawn curve is the linear least squares fit.

$$Z = V_{j,u}^o + \mu \log \left( \frac{6000 \pi A^2 Q}{M_m^2} \right) \quad (8c)$$

where Eqs. (3b), (4) and (7) have been used. It thus ensues

$$\Delta \in_{j,u} \sim M^{\gamma_{j,u}} \rho_p^{\mu_{j,u}} \quad \gamma_{j,u} = v_{j,u} + 2\mu_{j,u} \quad (9)$$

The following values for  $\gamma$  are thus found

$$\begin{aligned} \gamma_{1,a} &= (3.3 \pm 0.3) & C/C^* < 2.5 \\ \gamma_{1,b} &= (2.3 \pm 0.5) & C/C^* > 2.5 \\ \gamma_{2,a} &= (0.24 \pm 0.09) & C/C^* < 2.5 \\ \gamma_{2,b} &= -(0.12 \pm 0.05) & C/C^* > 2.5 \end{aligned}$$

In view of the relatively small magnitude of  $\Delta \in_2$  and related uncertainties as well as the closeness of the various  $V_2$  and  $\mu_2$  values, the significance of the exponents  $\gamma_{2,a}$  and  $\gamma_{2,b}$  must be appraised with caution. It cannot be excluded that the influence of the low frequency dispersion of much larger amplitude partially or even totally obscures the real concentration and molar mass dependence of  $\Delta \in_2$ . It is, to say the least, surprisingly coincidental that for the samples with  $M \geq 177\,000$  at comparable  $C$  this amplitude decreases with  $M$  while the amplitude of the low frequency dispersion increases considerably.

What seems to be established, however, is that the origins of the high frequency and the low frequency dispersion should be different.

## 5. The dielectric increments in the dilute regime

For the lowest molar mass  $M = 65\,000 \text{ g mol}^{-1}$  at least five concentrations investigated are below or around  $C_g^*$ , the yardstick for the separation between the dilute concentration regime and the transition region towards the semi-dilute one. For the solutions of this sample the values of  $\Delta \in_1$  are systematically lower than those of  $\Delta \in_2$  and quite small even above  $C_g^*$  (see Fig. 9). Therefore it may be appropriate to consider for  $M = 65\,000 \text{ g mol}^{-1}$   $\Delta \in = (\omega \rightarrow 0) - \infty$  as the quantity of interest instead of  $\Delta \in_1$  and  $\Delta \in_2$  separately (Fig. 9). The two samples of  $M = 88\,000$  and  $177\,000 \text{ g mol}^{-1}$ , respectively, also have  $\Delta \in_1 < \Delta \in_2$  and are small at concentrations around  $C_g^*$  (see Figs. 10 and 11 with values of  $\Delta \in$  included). In this dilute regime, moreover,  $\Delta \in$  of all three samples fall on one single line, an additional argument justifying the use of the total increment (Fig. 12). A linear least squares fit of  $\log(\Delta \in)$  against the scaled concentration ( $C/C_g^*$ ) produces the following equation:

$$\log(\Delta \in) = (1.38 \pm 0.02) + (0.46 \pm 0.03) \log \left( \frac{C}{C_g^*} \right)$$

$$C \leq C_g^*$$

Thus, the dielectric increment satisfies here a simple scaling relation

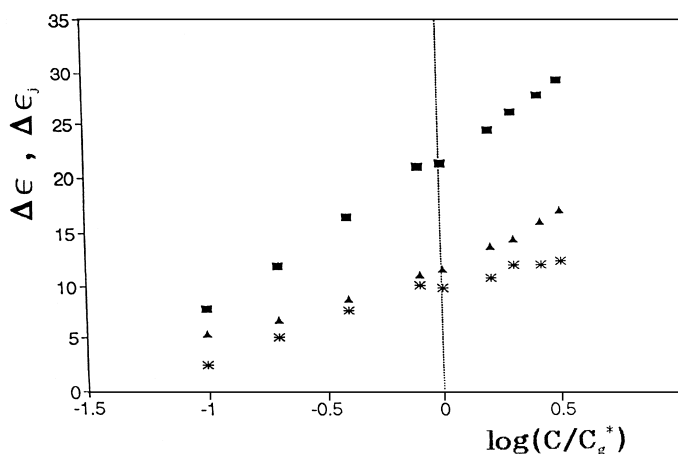


Fig. 9. Values of  $\Delta \in_1$  (\*),  $\Delta \in_2$  ( $\Delta$ ) and  $\Delta \in$  (■) around  $C_g^*$  for the solutions of  $M = 65\,000 \text{ g l}^{-1}$ .

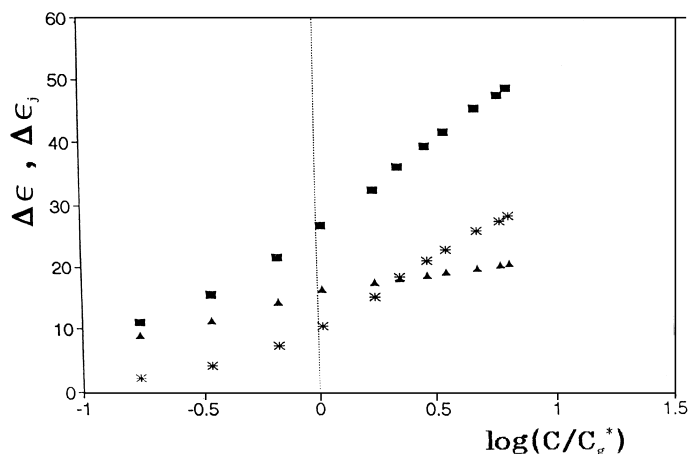


Fig. 10. Values of  $\Delta\epsilon_1$  (\*),  $\Delta\epsilon_2$  ( $\Delta$ ) and  $\Delta\epsilon$  (■) around  $C_g^*$  for the solutions of  $M = 88\,000\text{ g l}^{-1}$ .

$$\Delta\epsilon \sim M^0 \left( \frac{C}{C_g^*} \right)^\mu \sim M^\gamma \rho_P^\mu \quad (10a)$$

$$\mu \approx 0.46 \pm 0.3 \quad \gamma \approx \nu + 2\mu \approx 0.92 \pm 0.6 \quad (10b)$$

where Eq. (3a) has been used. The exponent of the molar mass power in the dilute regime is thus found to be close to unity, and that of the concentration dependence is close to 0.5.

The double Cole–Cole fit of the experimental points below and around  $C_g^*$  displays other ‘anomalies’ besides the small values of  $\Delta\epsilon_1 < \Delta$

$\epsilon_2$ . The two fitted relaxation times hardly differ more than one order of magnitude and the  $\beta$ -parameter for the low frequency dispersion is definitely higher than the average value of this parameter in the low frequency range of the other solutions. All this could suggest is that these solutions feature only one single dispersion region. In fact a fit of the experimental dielectric relaxation curve to a single Cole–Cole equation is statistically acceptable with a  $\beta$ -parameter close to the average values of  $\beta_1$  (see as an example Fig. 13). For the fit to a single Cole–Cole equation the standard deviation of the experimental points with respect to the fitted curve is  $\sigma_y = 0.15$

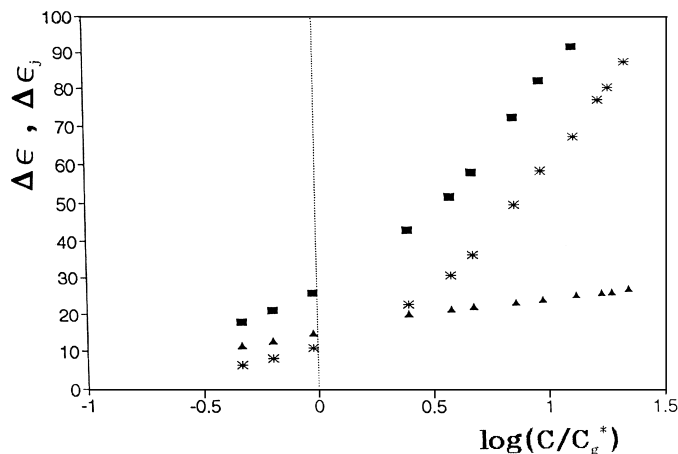


Fig. 11. Values of  $\Delta\epsilon_1$  (\*),  $\Delta\epsilon_2$  ( $\Delta$ ) and  $\Delta\epsilon$  (■) around  $C_g^*$  for the solutions of  $M = 177\,000\text{ g l}^{-1}$ .

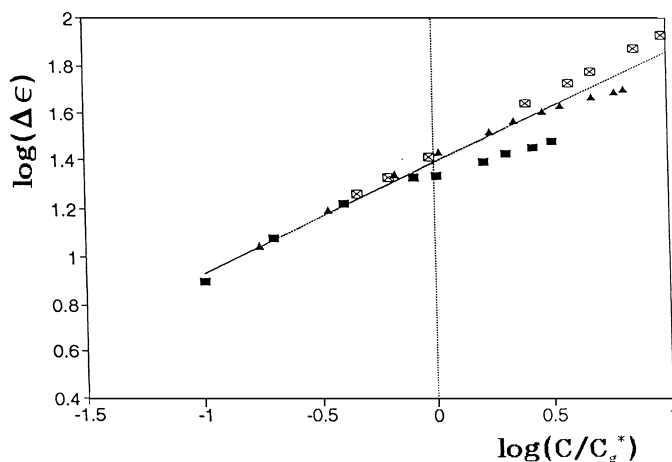


Fig. 12. Values of  $\Delta\epsilon$  around  $C_g^*$  for solutions of the three samples with lowest molar mass  $M = 65\,000$  (■),  $88\,000$  (△) and  $177\,000$  (□)  $\text{g mol}^{-1}$ . The drawn curve is the linear least squares fit to all the points at  $C/C_g^* \leq 1$ .

units against  $\sigma_y = 0.07$  for the fit to two Cole–Cole equations. The latter with seven adjustable parameters is somewhat better than the former for which only four adjustable parameters are needed, however. But both values of  $\sigma_y$  are well within the range of experimental accuracy. Moreover, as pointed out before, the fit to a Cole–Cole equation has not necessarily to be impeccable as it remains an empirical expedient.

Possibly we have here a common trend for

solutions in the dilute regime where the more or less completely stretched polyelectrolyte chains with negligible interactions could be characterized by dispersion curves featuring only one single relaxation region.

## 6. Concluding remarks

Although this empirical scaling analysis of the

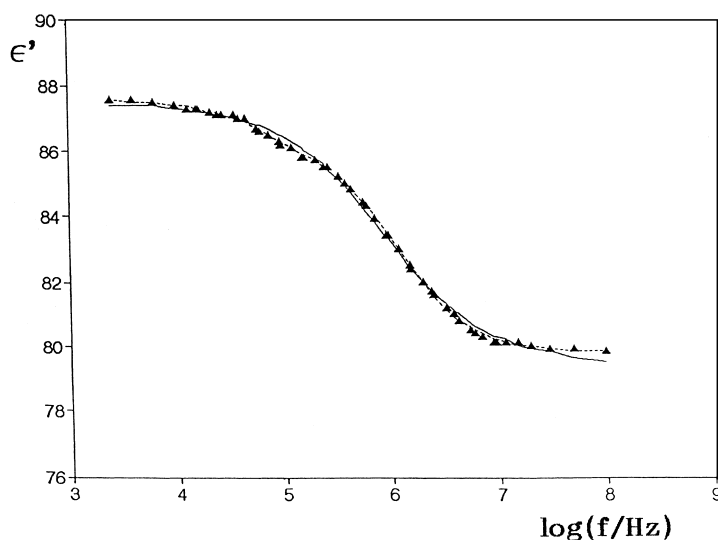


Fig. 13. The dispersion curve of the aqueous  $C = 0.071 \text{ g l}^{-1}$  solution of the sample  $M = 65\,000 \text{ g mol}^{-1}$ . The experimental points (··) are fitted with a double Cole–Cole (··) and a single (—) Cole–Cole equation.

dielectric increments of the various NaPSS solutions in water does not disclose anything about the relaxation mechanism(s) it has, at least, clearly revealed that there are important concentration effects to consider. In the concentration range above the dilute regime the increments of both the low and high frequency dispersion show a change in the concentration and molar mass dependence around the characteristic  $C^*$  concentration. This  $C^*$  has been advanced by Odijk as the concentration around which for a polyion of sufficient length flexibility effects of the polyelectrolyte chain start to influence its behavior. The fact that the dissimilarity between low and high concentration region appears at a somewhat higher value than the  $C^*$ -value proposed by Odijk (approx.  $C \approx 2.5 C^*$ ) does not invalidate the existence of this yardstick. It is probably due to the various approximations introduced in the estimate of this characteristic concentration. The remarkable fact remains that for all samples but the lowest molar mass the change of concentration dependence of the dielectric increments occurs around the same reduced concentration ( $C/C^*$ ) and that a shift along the y-axis causes all the curves to coincide, thus providing support for the existence of a characteristic concentration around  $C^*$ .

It is not surprising that there is a difference in molar mass dependence between the two concentration regimes. At present, and in the absence of a theory for the dielectric properties as function of the concentration, there is no simple explanation for the actual values for the molar mass exponents  $\gamma$  which have been observed. The negative value of  $\nu'$  for  $\Delta \in_2$  in both concentration ranges should be considered with caution, as discussed above.

The near absence of a concentration dependence of  $\Delta \in_1$  and  $\Delta \in_2$  at  $2.5 C^* < C < C^{**}$  is more startling. Possibly two opposing effects are responsible for this feature. As the values of  $\in_\infty$  do not drop below the relative permittivity of the solvent it is unlikely that it is caused by a decrease of the solvent polarization. Perhaps it is related to some aggregation phenomena, the occurrence of which is still a matter of discussion, however.

Below and around  $C_g^*$  the existence of one single dispersion region seems to be a reasonable conjecture. It suggests that the high frequency dispersion correlates with polyion interaction effects as they appear above  $C_g^*$ .

Both the concentration and molar mass dependences of the total dielectric increment in this concentration regime are different from those of either  $\Delta \in_1$  or  $\Delta \in_2$  at higher concentrations whether below or above Odijk's  $C^*$ . Extrapolation of data from above  $C_g^*$  to dilute conditions is therefore improper and can not give meaningful results.

A final remark concerns the influence of low molar mass salt on the dielectric properties of polyelectrolyte solutions. Preliminary measurements have shown a striking effect of already small salt concentrations  $C_s$ . For  $M = 780\,000 \text{ g mol}^{-1}$  a NaCl concentration of  $10^{-4} \text{ mol l}^{-1}$  in a  $C = 0.172 \text{ g l}^{-1}$  solution (corresponding to a total counterion concentration of approx.  $8 \times 10^{-4} \text{ mol l}^{-1}$ ) reduces  $\Delta \in_1$  by a factor of 2.4 but hardly affects  $\Delta \in_2$ , however. Increasing at the same  $C > C_g^*$  the salt concentration to  $C_s = 2 \times 10^{-3} \text{ mol l}^{-1}$  causes practically a collapse of  $\Delta \in_1$  to a value 43 times smaller than in the absence of the salt and comparable to the amplitude of  $\Delta \in_2$ . Changes in average conformation and size as well as reduction in the charge interactions between polyions may be held responsible for these large effects. It cannot be excluded that also the mechanisms responsible for the dielectric response are affected by the addition of salt.

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