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A quantitative description of the viscometric behaviour of partially neutralized poly(acrylic acid) in aqueous solutions studied by the isoionic dilution method

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The intrinsic viscosity, $[\eta]$, and the Huggins constant, k', of a poly(acrylic acid) (PAA) sample have been measured at different degrees of neutralization, i, ranging from $i = 0.25$ to $i = 1.00$ and different ionic strengths, I, in the region 1.0×10^{-4} M $< I < 1.0 \times 10^{-1}$ M, using the isoionic dilution method in aqueous solutions. The results show that the variations of $[\eta]$ and k' as a function of I are given by scaling laws characterized by constant exponents irrespective of the i value of the PAA sample investigated. An empirical equation giving the reduced viscosity of the PAA sample as a function of its concentration for various values of i and I has been obtained.

(Keywords: poly(acrylic acid); isoionic dilution; polyelectrolyte)

INTRODUCTION

We have recently studied the intrinsic viscosity ($[\eta]$) of partially neutralized poly(acrylic acid) (PAA) in aqueous solution[1] by using the isoionic dilution method[2,3]. We observed the existence of a scaling relation between $[\eta]$ and the ionic strength (I) of the solvent used. Similar behaviour was also observed for the Huggins constant (k').

We report here the measurements of $[\eta]$ and k' of the same PAA sample with different neutralization degrees (i) in the ionic strength region $I = (1.0 \times 10^{-1})$–$(1.0 + 10^{-4})$M NaCl. The results are represented by an empirical equation giving the reduced viscosity (η_{sp}/c) of the polyelectrolyte sample used as a function of its concentration (c) for the different values of i and I.

EXPERIMENTAL

The PAA sample used was a 25 wt% solution from Polysciences. The procedures followed for its purification, characterization and partial neutralization with NaOH have been described elsewhere[1]. Its $\overline{M}_v$ was found to be equal to 94 000 in the sodium salt form. The viscosity measurements were carried out at 30°C using an Ubbelohde dilution viscometer, as has also been previously described[1].

RESULTS AND DISCUSSION

Viscosity measurements by the isoionic dilution method have been carried out with the above-mentioned PAA sample partially neutralized at different degrees of neutralization i ($i = 0.25$, 0.35, 0.50, 0.75 and 1.00) and different I. The ionic strength of the NaCl/water solution used for dilution of the initial polymer solution has been calculated through the predictions of Manning's theory[4] for the values of the counterion activity coefficient, which are in close agreement with the results from membrane equilibrium experiments[5]. In our previous work[1] we have found that for $i > 0.2$ the ratio of the Na^+ ion concentration in the solvent used for dilution purposes to the Na^+ concentration of the partially neutralized PAA water solution coincides with the value given by the Manning's theory for the Na^+ ion activity coefficient for each value of i. The reduced viscosity (η_{sp}/c) so measured for each partially neutralized PAA sample, at different I, obeys the linear Huggins equation

$$(\eta_{sp}/c) = [\eta] + k'[\eta]^2 c \tag{1}$$

The dependence of $[\eta]$ and k' on I for the above-mentioned samples at different i, is shown in *Figures 1* and *2*, respectively, through double logarithmic plots. The results are well represented by straight lines expressed by the equations:

$$[\eta] = aI^{-b} \tag{2}$$

$$k' = a'I^{-b'} \tag{3}$$

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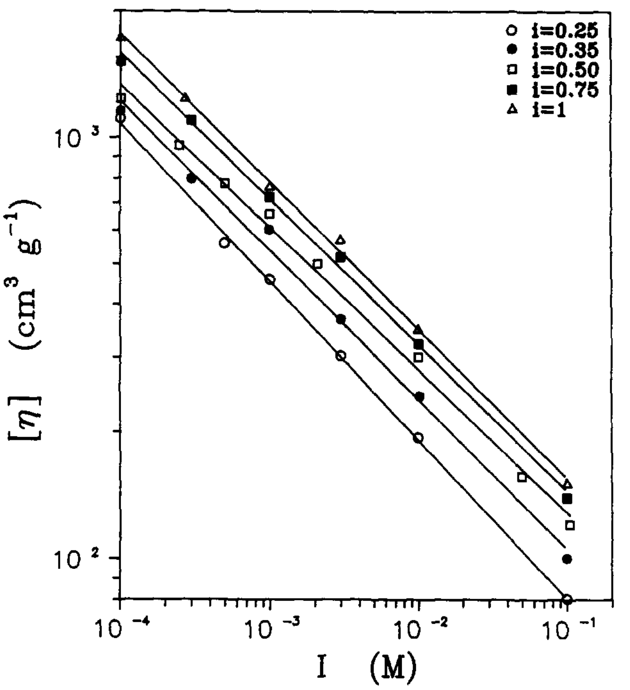

Figure 1 Intrinsic viscosity, $[\eta]$, *versus* ionic strength, I, for a PAA sample at different neutralization degrees, i

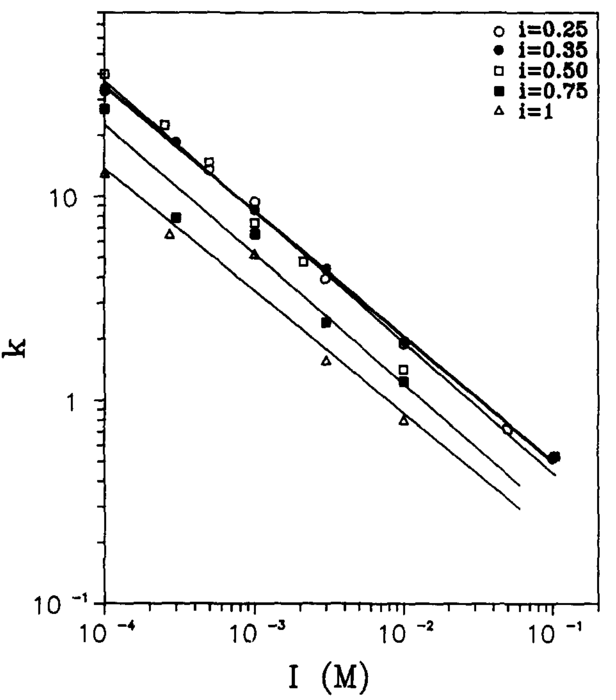

Figure 2 Huggins coefficient k', *versus* ionic strength, I, for the same samples as in *Figure 1*

where a, a', b and b' are parameters characteristic of the polyelectrolyte sample investigated and probably dependent on i. From *Figures 1* and *2* or equations (2) and (3) respectively it is seen that $[\eta]$ and k' increase as I decreases. The behaviour of $[\eta]$ is expected and is explained by the decrease of the charge shielding of the chain by the counterions as I decreases. The behaviour of k' has also been observed elsewhere[1,6,7]. It could be explained by the appearance of mutual electrostatic attractions between the negatively charged polymer chains through their attractions with the positively charged free counterions[8,9]. Nevertheless this behaviour has also been attributed to the 'secondary' electroviscous effect[7], expressing the energy dissipation through the collisions of the polyelectrolyte coils characterized by the existence of a double layer which expands as I decreases. Both the above approaches explain the considerable increase of the reduced viscosity with the concentration of the polyelectrolyte, especially at low ionic strength.

From the slopes of the practically parallel straight lines in *Figures 1* and *2* we have obtained the values of the exponents b and b' which are equal to 0.35 and 0.62, respectively. The values of these exponents do not depend on the degree of neutralization of the polyacid, i.e. on the charge density of the macromolecular chain. They probably depend on the backbone chain rigidity. The deviation of the intrinsic viscosity exponent $b = 0.35$ from the value 0.50 found in the earlier work of Noda *et al.*[10] is probably due to the fact that they have worked in the higher ionic strength region, $I = (5.0 \times 10^{-1})$–(1.0×10^{-2})M. Moreover, it seems that they have not obtained really linear Huggins plots, especially in the lower ionic strength region. In our work, in contrast, by using the isoionic dilution, we have obtained linear Huggins plots even in the very low ionic strength region, $I = 1.0 \times 10^{-4}$ M. The parameters a and a' are, on the contrary, strongly dependent on i, as is shown in *Figures 3* and *4*, where a and a' have been plotted as a function of i^{-1} and i, respectively. The observed linear relations are described by the equations:

$$a = 82 - 12.0 i^{-1} \tag{4}$$

$$a' = 0.151 - 0.102 i \tag{5}$$

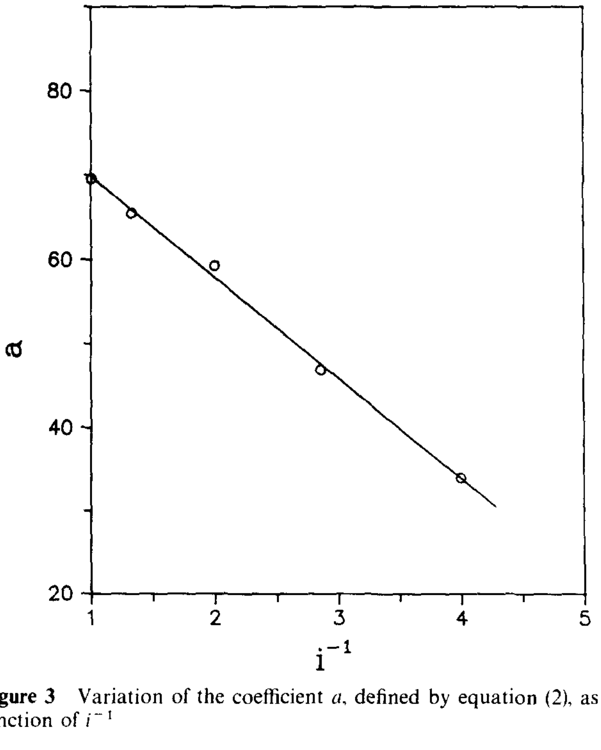

Figure 3 Variation of the coefficient a, defined by equation (2), as a function of i^{-1}

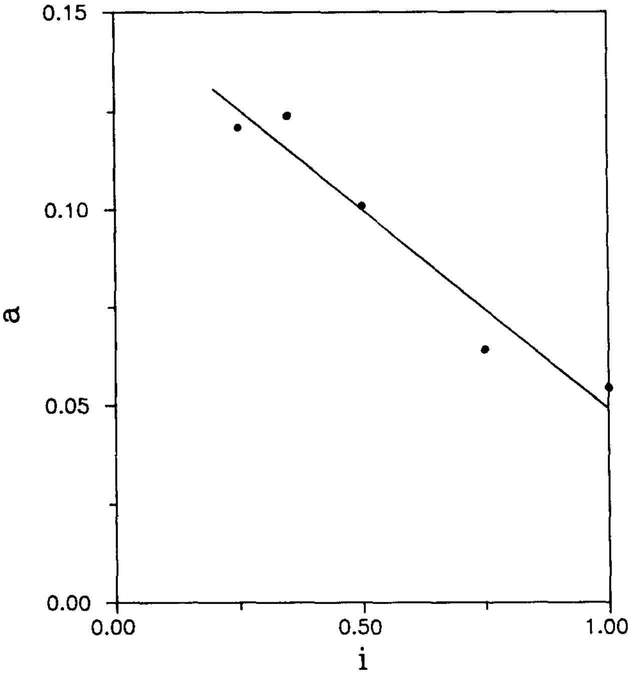

Figure 4 Variation of the coefficient a', defined by equation (3), as a function of i

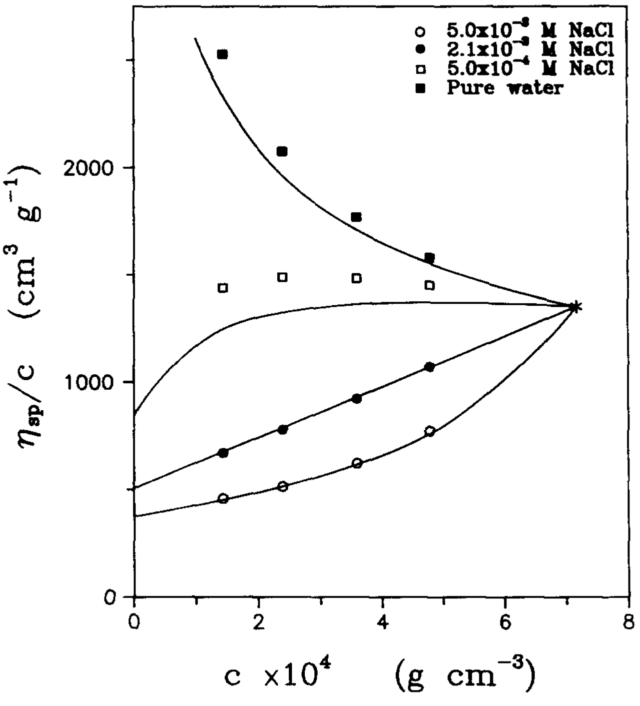

Figure 5 The viscometric behaviour of a PAA sample with $i=0.50$ for different salt concentrations of the dilution solvent. The points represent the experimental results while solid lines have been plotted using equation (6). The solvent used for the initial PAA solution (*) is pure water. Straight line (●) represents the isoionic dilution procedure for this sample

From equation (4) we can conclude that $[\eta]$ increases as i increases, for constant I, while, as is shown by equation (5), k' decreases as i increases, for constant I. This behaviour for $[\eta]$ is explained by the increase of the charge density of the chain, as i increases, resulting in an expansion of the polyelectrolyte chain. The observed behaviour of k' suggests a decrease of interpolymer interactions as i increases. An explanation for this behaviour could be deduced from Manning's theory[4] of counterion condensation. According to this theory the counterion activity coefficient, equations (8) and (9), decreases as i increases. This decrease could be related to a corresponding weakening of the interchain attractive interactions or to the formation of a stronger double layer which does not favour energy dissipation through interparticle collisions.

By substitution of the values of $[\eta]$ and k', as they are given by equations (2) and (3), into equation (1) we obtain the empirical equation

$$(\eta_{sp}/c)=(82-12.0\mathrm{i}^{-1})I^{0.35} \\ +(0.151-0.102\mathrm{i})(82-12.0\mathrm{i}^{-1})^2 I^{-1.32}c \qquad (6)$$

giving the reduced viscosity of the partially neutralized PAA sample as a function of c for every i and I. We have to point out here that I expresses the counterion activity of the polyelectrolyte and it is calculated according to Manning's formulation[4] by the equation

$$I=\gamma_1(n_p+n_s) \qquad (7)$$

where n_p is the concentration of the polymer counterions and n_s of the salt (NaCl). γ_1 is the total counterion activity coefficient given by the equation

$$\gamma_1=\frac{\xi^{-1}x+1}{x+1}\mathrm{e}^{\frac{-\frac{1}{2}\xi^{-1}x}{\xi^{-1}x+2}} \qquad \text{for } \xi>1 \qquad (8)$$

or by the equation

$$\ln\gamma_1=-\frac{1}{2}\xi\frac{x}{x+2} \qquad \text{for } \xi<1 \qquad (9)$$

where $\xi=2.85i$ for vinylic polymers and $x=\frac{n_p}{n_s}$.

Figure 5 presents some experimental results for η_{sp}/c of PAA with $i=0.50$ as a function of the concentration c of the polyelectrolyte. The solvent used for dilution of the initial aqueous polyelectrolyte solution was a NaCl solution at different concentrations.The lines have been drawn according to equation (6). We observe a very good agreement between the experimental points and the predictions of equation (6).

CONCLUSIONS

The use of the isoionic dilution method in the viscometric study of a partially neutralized weak polyelectrolyte, PAA, at different i, has shown the existence of scaling laws describing the variation of $[\eta]$ and k' as a function of I. The exponents of these scaling laws are constant while their coefficients depend on i. The above results are in agreement with previously reported results suggesting the existence of order in polyelectrolyte dilute solutions[11], as well as with an older explanation[5] based on the existence of the secondary electroviscous effect.

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