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Chain conformation and intermolecular interaction of partially neutralized poly(acrylic acid) in dilute aqueous solutions

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Abstract

The isoionic dilution method was used to measure the intrinsic viscosity, [η], and the Huggins coefficient, K_H, of two poly(acrylic acid) samples, 50% neutralized with NaOH, with molecular weights 5.0×10^3 (Na50PA5) and 4.8×10^4 (Na50PA48) at different ionic strengths. For Na50PA5 at low ionic strength, [η] is higher than the value predicted by a rigid-rod model. Assuming that the chain has reached its maximum extension, we have combined the rigid-rod model with the idea of effective dimensions that depend linearly on the Debye–Hückel screening length, κ^{-1}, to account for a primary electroviscous effect, as a means to describe the observed behavior. As a consistent approach, we have also combined the effective dimensions with the wormlike chain model to calculate the persistence length of the higher molecular weight sample, Na50PA48. The result is that the electrostatic persistence length, l_e, is proportional to κ^{-1}, in the region of high to moderate ionic strength, as is usually observed experimentally for flexible polyelectrolytes, while at the lowest ionic strengths, l_e tends to level off, which was predicted theoretically. Both the samples show a considerable increase in the Huggins coefficient as the ionic strength is lowered, with the sample having the lowest molecular weight giving the highest value at any particular ionic strength. This is attributed to the increasing intermolecular electrostatic interactions, which have a relatively larger importance in the case of Na50PA5, because the dimensions of the chain are smaller when compared with the range of the electrostatic interactions, as measured by κ^{-1}, than for Na50PA48.

Keywords: Partially neutralized poly(acrylic acid); Polyelectrolytes; Intrinsic viscosity

1. Introduction

There is a considerable controversy regarding the nature of the polyelectrolyte effect (increase of the reduced viscosity with decreasing concentration) and the behavior of polyelectrolytes in a dilute solution [1,2]. Besides the traditional explanation in terms of a conformational coil–rod transition with increasing Debye–Hückel screening length, κ^{-1}, (decreasing ionic strength, I) due to *intra*molecular electrostatic interactions [3], there are other theories, which attempt to explain this effect through *inter*molecular electrostatic interactions [4–7]. The latter has been supported by viscosity measurements of relatively low molecular weight polyelectrolytes [8], low shear viscometric results [9], and viscosities of aqueous suspensions of charged spheres [10–12]. Nevertheless, support for the conformational interpretation still remains [13].

The conformational approach to polyelectrolyte behavior in solution consists mainly of analysing the macromolecular chain in terms of the persistence length, q, which is a measure of stiffness and equals half the Kuhn segment length for wormlike chains according to the Kratky–Porod model [14]. It has become a common practice to divide q into a bare part, l_0, due to the rigidity of the chain backbone, and an electrostatic part, l_e, arising from the repulsion between charges on the polyelectrolyte chain as follows:

$$q = l_0 + l_e. \tag{1}$$

Odijk [15] and independently, Skolnick and Fixman [16] (OSF) derived equivalent models to calculate the influence of ionic strength on the electrostatic persistence length. The OSF result, suggesting a quadratic dependence on κ^{-1} for l_e when the Debye length is much shorter than the contour length, has been confirmed for intrinsically stiff polyelectrolytes, like DNA [17], but it does not agree with the experimental results for flexible polyelectrolytes, which show a linear relationship, $l_e \propto \kappa^{-1}$ [18–21]. There had been suggestions, based on Monte Carlo simulations, that

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the electrostatic persistence length does not depend on the Debye length in any simple and consistent manner [22,23]. However, recent simulations have shown that this is a matter of definition [24]. If l_e is defined in a way that is related to what is observed experimentally, simulations do indeed give a near linear dependence on κ^{-1}, as reported earlier [25,26]. As we are dealing with experimental results here, we will simply treat the persistence length as an experimental observable (operationally defined) and not question whether this is consistent with the underlying assumptions or not [23].

In this work we have used the isoionic dilution method [27,28] to measure the intrinsic viscosity, [η], and the Huggins coefficient, K_H, of poly(acrylic acid) 50% neutralized with NaOH and we have covered a relatively broad ionic strength region going down to $I = 2.0 \times 10^{-4}$ M, which is wider than the region treated by Tricot [18], where a lowest value of $I = 2.5 \times 10^{-3}$ M was attained in the usual dilution procedure. We have used samples of two different molecular weights, to be able to compare their properties. By using the hydrodynamic wormlike chain theory of Yamakawa [29], to describe the intrinsic viscosity of the higher molecular weight sample and the rigid-rod model [30,31], for the lower molecular weight, we were able to study the effect of charge screening on the chain stiffness. We have proposed a new approximation for the chain diameter and the chain contour length, as a function of the Debye length, to explain the viscosity results at lower ionic strengths, particularly for the lower molecular weight sample.

2. Experimental

2.1. Materials

Two poly(acrylic acid) samples were used. The low molecular weight sample, with a nominal molecular weight equal to 5000 was purchased from Aldrich as a 50 wt.% solution in water. The higher molecular weight sample of a nominal molecular weight equal to 50 000 was purchased from Polysciences as a 25 wt.% solution, in water also. They were neutralized with NaOH in slight excess and purified by dialysis and lyophilized. A known quantity of each of the products obtained was 50% neutralized with HCl and purified by dialysis for complete removal of the salt and lyophilized. The molecular weights of the samples were estimated through viscosity measurements of the fully neutralized samples in KBr 1.5 M at 15°C according the equation $[\eta] = 1.25 \times 10^{-2} M^{0.5}$ ([η] in $cm^3\,g^{-1}$) [32], and were found to be equal to 5.0×10^3 (Na50PA5) and 4.8×10^4 (Na50PA48), respectively, in the 50% neutralized form.

2.2. Viscometry

The viscosity measurements were carried out at 30°C using an automated viscosity measuring system (AVS 300, Schott Geräte, Germany) equipped with an Ubbelohde dilution viscometer. The precision of the measurements was 0.01 s and the reproducibility was 0.02 s. Kinetic energy corrections were taken into account. Water used as the solvent was taken from a Seralpur Pro 90 C apparatus (Germany).

The dilutions to measure [η] and K_H were made so that the ionic strength, I, of the diluent was the same as that of the polyelectrolyte solution, following the isoionic dilution method [27,28]. To estimate the ionic strength of the polyelectrolyte solution, I was expressed as the total counter ion activity:

$$I = \gamma_1(n_p + n_s), \tag{2}$$

where γ_1 is the activity coefficient of the counterion, n_p the molar concentration of counterions from the polymer and n_s the concentration of added salt (NaCl). According to the Manning theory [33] the activity coefficient is given by:

$$\gamma_1 = \frac{\xi^{-1}x + 1}{x + 1}\exp\left[-\frac{(1/2)\xi^{-1}x}{\xi^{-1}x + 2}\right] \qquad \text{for } \xi > 1, \tag{3}$$

where $x = n_p/n_s$. ξ is the Manning parameter given as:

$$\xi = \frac{e^2}{4\pi\epsilon k_B T b} = \frac{l_B}{b}, \tag{4}$$

where e is the elementary charge, ϵ the permittivity, k_B Boltzmann's constant, T the absolute temperature and b the charge spacing. $l_B = e^2/4\pi\epsilon k_B T$ the Bjerrum length, which corresponds to a distance where the electrostatic and thermal energies balance. In water at 25°C, the Bjerrum length is about 7.16 Å and for partially charged vinylic polymers, for which the charge spacing is calculated as $b = b_0/i$, where b_0 is the monomer projection length equal to 2.52 Å and i the degree of neutralization, 0.50 in this work, ξ is given by:

$$\xi = 2.84i. \tag{5}$$

In salt-free solutions Eq. (3) is reduced to:

$$\gamma_1 = \xi^{-1}e^{-1/2}, \qquad \xi > 1. \tag{6}$$

The same procedure was followed to determine the ionic strength for the dilution with a NaCl solution in Ref. [34]. We have employed the isoionic dilution method [27,28], where the polyelectrolyte solution is diluted with a salt solution of the same (effective) ionic strength in order to achieve a stable conformation throughout the dilution. This was observed by Moan and Wolff in neutron scattering experiments [35]. A recent simulation study has also shown that Eq. (2) is a valid formulation when the chain conformations are to be kept more or less constant [36]. The simulations also indicate that although Eqs. (3) and (6) are not generally applicable, they can be used to predict γ_1 for solutions of vinylic polyelectrolytes at the present concentrations.

We should point out that our viscosity measurements were limited to $I > 2.0 \times 10^{-4}$ M for Na50PA48 because of an instability that appears at very low ionic strengths. For

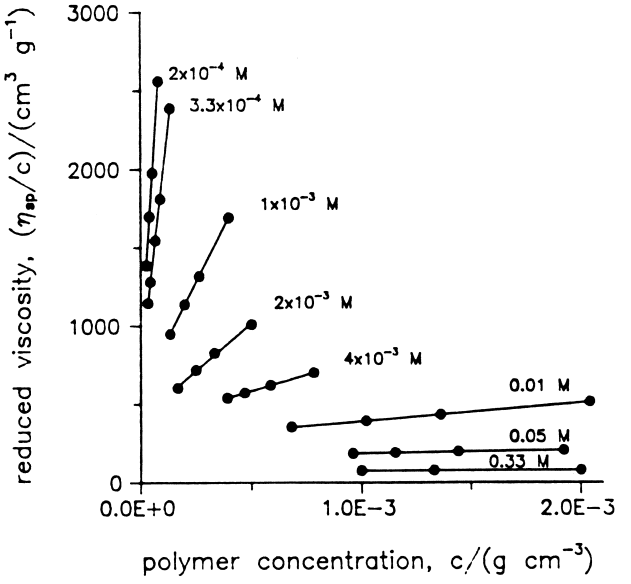

Fig. 1. The Huggins plots of Na50PA48 in water, isoionically diluted with NaCl solutions at different ionic strengths.

the lower molecular weight sample, Na50PA5, we have confined our measurements to $I > 1.0 \times 10^{-3}$ M because at lower ionic strengths the solution viscosity, η, is too close to the solvent viscosity, η_0, and the experimental error in the determination of the specific viscosity, $\eta_{sp} = (\eta - \eta_0)/\eta_0$, becomes unacceptable.

3. Results and discussion

The reduced viscosity, $[\eta]_{sp}/c$, for Na50PA5 and Na50PA48, measured according to the isoionic dilution method, obeys the linear Huggins equation:

$$\frac{\eta_{sp}}{c} = [\eta] + K_H[\eta]^2 c, \tag{7}$$

where c is the mass concentration of the polyelectrolyte.

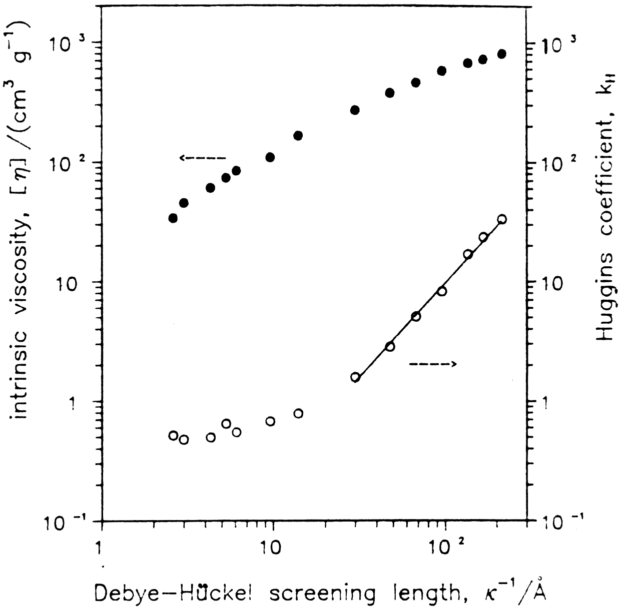

Fig. 2. The intrinsic viscosity, $[\eta]$, (●) and the Huggins coefficient, K_H, (○) of Na50PA48 as functions of the Debye–Hückel screening length, κ^{-1}.

The results obtained for the Na50PA48 sample at different ionic strengths, 2.0×10^{-4} M $< I < 1.4$ M, are shown in Fig. 1. As can be seen, good, straight lines were obtained in the isoionic dilution and the slopes increased for $I < 0.01$ M. At very low ionic strength, the slope becomes extremely high, but here the measurements also start becoming unpredictable. This is probably related to the concentration fluctuations or aggregate formation [20].

The Debye–Hückel screening length, κ^{-1}, which is directly related to the range of the electrostatic interactions, is given by $\kappa^2 = 8\pi l_B N_A I$ in SI units, where N_A is Avogadro's number. Thus the screening length is inversely proportional to the square root of the ionic strength and the equation can be transformed into:

$$\kappa^{-1} = 3.04 I^{-1/2}, \tag{8}$$

which gives κ^{-1} in Å, if I is expressed in units of mol/l. To be specific, in Debye–Hückel theory the screening length is defined by $I = \frac{1}{2}\Sigma_k z_k^2 n_k$, where z_k and n_k are the charge and concentration of species k, respectively. In this article, I is generally the effective ionic strength, approximated via Eq. (2), and κ^{-1} derived from it does not necessarily have exactly the same physical interpretation as the original Debye length, but in the following discussion this difference will be neglected.

The values of $[\eta]$ and K_H obtained for Na50PA48 at different values of I are plotted in Fig. 2 as a function of the screening length, κ^{-1}. From the results it is apparent that $[\eta]$ increases with κ^{-1} from the value $[\eta] = 34.0\ cm^3\ g^{-1}$, corresponding to a nearly ideal coil conformation, to the value $[\eta] = 810\ cm^3\ g^{-1}$, corresponding to an extended, nearly rodlike conformation. K_H, which is a measure of intermolecular interactions, remains lower than 1 for $\kappa^{-1} < 20$ Å ($I > 2.3 \times 10^{-2}$ M), which implies the presence of only weak intermolecular interactions, comparable to those usually encountered in non-polar polymer–solvent systems. As κ^{-1} exceeds the value of 20 Å, K_H increases sharply taking the value of 34 at $\kappa^{-1} = 215$ Å. A similar behavior of K_H has also been observed in potassium poly(styrenesulfonate) solutions [37].

As the Debye length becomes comparable to the size of the molecule, the intermolecular electrostatic interactions should become important and most probably be observed as a secondary electroviscous effect due to inter-chain repulsion. Russel has shown that a classical hard-sphere system corresponds to a minimum in the Huggins coefficient and that an extra pair-potential can increase K_H quite substantially [38]. For example, making the radius corresponding to the distance of closest approach larger than the bare or hydrodynamic radius, R_H, which determines the intrinsic

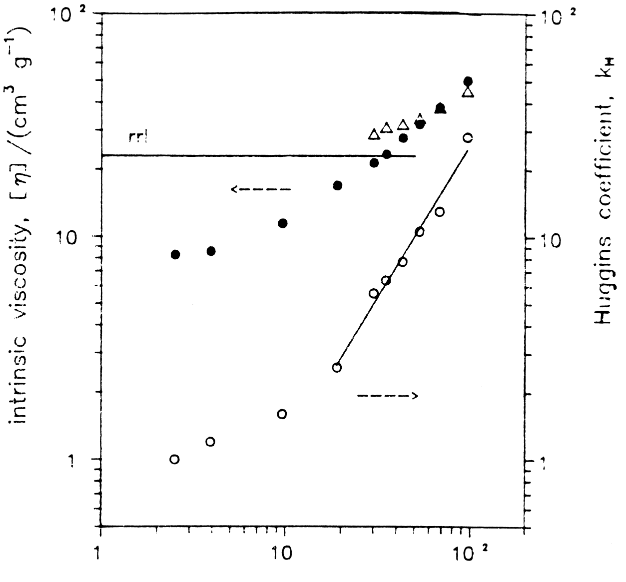

Fig. 3. The intrinsic viscosity, [η], (●) and the Huggins coefficient, K_H, (○) of Na50PA5 as functions of κ^{-1}. The [η] values calculated for a rodlike chain with the diameter and the contour length depending on κ^{-1}, according to Eqs. (12) and (13), are also given (△) in the ionic strength region where a rodlike behavior would be expected.

viscosity, Russel found K_H to be proportional to the ratio of the two radii raised to the power of five. A similar factor, with κ^{-1} as a measure of the range of the electrostatic interactions, appears in his treatment of charged spheres, although it is partly counterbalanced by a complex function of κ, R_H and other parameters of the system, for example the charge, z, i.e. $K_H \propto F(z,\kappa,R_H)/(\kappa R_H)^5$ [4]. The ratio between the range of interactions and hydrodynamic radius is thus an important factor, although it is not the only one in the case of electrostatic interactions.

This treatment of solutions of charged spheres, like that of Hess and Klein [5] (discussed later) and the consideration of rodlike polyelectrolytes by Rabin and others [6,7], is based on intermolecular, electrostatic repulsion. A net Coulombic attraction between the particles, mediated by the counterions has also been suggested [39,40]. This could in principle also explain the high K_H values for $\kappa^{-1} > 20$ Å, although the arguments for a net attraction have a questionable basis [41–44], especially in the case of monovalent counterions [45].

Fig. 3 shows [η] and K_H as functions of κ^{-1} for the lower molecular weight sample, Na50PA5. We see that the Huggins coefficient, K_H, is now displaced to a higher value at a given κ^{-1} compared to the results for the sample with the higher molecular weight, as shown in Fig. 2. For example, at $\kappa^{-1} = 10$ Å K_H equals 1.6 for Na50PA5 and 0.7 for Na50PA48 and at $\kappa^{-1} = 96$ Å the values are 28 and 8, respectively. Thus we conclude that the interchain interactions have a stronger effect for the lower molecular weight polyelectrolyte.

From the aforementioned discussion about K_H increasing with an increasing ratio between the range of interactions and the hydrodynamic radius, it is tempting to rationalize the experimental observation with the fact that Na50PA5 has a smaller chain size than Na50PA48 and is therefore also smaller in comparison with the range of interactions, measured by κ^{-1}. However as already indicated, the range is not enough. We should also consider the strength of the interaction and this is expected to be weaker for the smaller molecule, as it contains less charge, z.

Hess and Klein have derived an expression for the electrostatic contribution to the viscosity of Brownian spheres using a weak coupling approximation [5]. This expression corresponds to the second term in the Huggins equation (Eq. (7)) and, together with $[\eta] \propto R_H^3/M$, it leads to $K_H \propto z^4/(\kappa^3 R_H^5)$. As z is proportional to the molecular mass, M, at a given degree of ionization, this suggests that K_H decreases with the increasing molecular weight (given κ^{-1}) as long as R_H grows faster than $M^{0.8}$. Cohen et al., have modified the theory in the case of strong coupling [7]. As a result the power of z is reduced to 2 and R_H has to grow faster than $M^{0.4}$, which means that even ideal coils ($R_H \propto M^{0.5}$) are expected to show a smaller Huggins coefficient when the molecular weight is increased. In our case, the apparent hydrodynamic radius, calculated from the intrinsic viscosity, grows as $M^{0.7}$. The expression derived by Russel [4] does not lend itself to such a simple analysis, but under the present conditions, it also leads to a smaller Huggins coefficient for the larger particle. For clarity, we should perhaps mention that the situation for flexible polyelectrolytes is expected to be further complicated by, among other things, the fact that an effective hydrodynamic radius will depend on κ^{-1}, as indicated by the ionic strength dependence of the intrinsic viscosity.

In order to further elucidate the observed viscometric behavior, we have treated the results according to the Yamakawa theory for the intrinsic viscosity of wormlike chains [29]. According to this theory, [η] is given as a function of the persistence length, q, by the equation:

$$[\eta] = \Phi(2q/M_L)^{3/2}M^{1/2}, \tag{9}$$

where M_L is the mass per unit length given by the ratio of the molecular weight of the monomer unit of the 50% neutralized NaPAA, $m = 83$, and the projection length of the vinylic monomer, $b_0 = 2.52$ Å. M is the total molecular weight of the polyelectrolyte. The parameter Φ is a function of the contour length, $L = M/M_L$, and the diameter, d, of the chain and takes the value 2.86×10^{23} in the non-draining Gaussian-coil limit. d has been calculated to be 5.8 Å from the partial molar volume data [46] from the equation of Tsuji et al. [47]:

$$d = \left(\frac{4vM_L}{\pi N_A}\right)^{1/2}, \tag{10}$$

where v is the partial specific volume of 50% neutralized

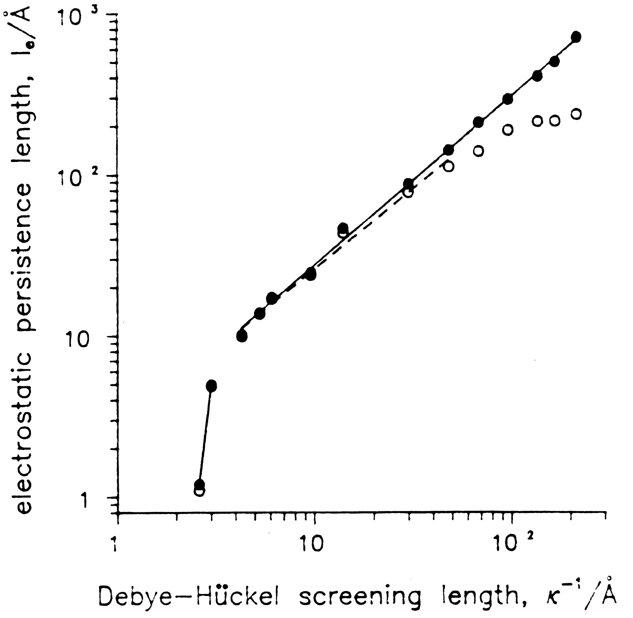

Fig. 4. The electrostatic persistence length, l_e, of Na50PA48 based on the molecular dimensions (●) and with the diameter and the contour length as functions of κ^{-1} according to Eqs. (12) and (13) (○).

poly(acrylic acid), $v = 0.484$ cm^3 g^{-1}. Φ is given in Tables 1 and 2 of Ref. [29] as a function of the reduced values of L and d relative to the Kuhn statistical segment length.

We have calculated q for Na50PA48 at different ionic strengths. In order to obtain the corresponding electrostatic persistence length, l_e, we have used Eq. (1) with a bare persistence length, l_0, of 11 Å as calculated from the value $[\eta] = 30.0$ cm^3 g^{-1} measured for Na50PA48 in 1.5 M NaCl solution at 15°C, which is considered to be the Θ solvent for this polymer [32]. This is comparable to the value of 12 Å calculated by Tricot [18] for sodium polyacrylate or 8–14 Å measured by small-angle X-ray scattering [48].

In Fig. 4, l_e vs κ^{-1} was drawn. We see that after an intersection point at $\kappa^{-1} = 3$ Å, where the screening length is of the same size as the separation between neighbouring monomers, l_e varies as κ^{-p} with $p = 1.05$, which is similar to the behavior normally observed for flexible polyelectrolytes [18–21]. Simultations have shown that intramolecular electrostatic interactions based on the Debye–Hückel approximation, are enough to generate the linear relationship [24–26], provided the bare persistence length is not much larger than the Debye length. OSF theory deals with intrinsically very stiff chains and predicts $p = 2$ [15,16], which obviously does not agree with the results for flexible polyelectrolytes. For $\kappa^{-1} < 3$ Å, the chain conformation reduces to that resulting only from the intrinsic, short range interactions found in a neutral polymer.

Analysing the viscosity behavior of the lower molecular weight sample, Na50PA5, according to the procedure of Yamakawa presents some difficulties. Resulting from the shortness of the chain, the values of Φ given in Tables 1 and 2 of Ref. [29] are almost outside the lower boundary, which means that a relatively accurate calculation of the persistence length from viscosity measurements seems to be difficult here. Moreover, this short chain is expected to be stretched to its maximum extension already at moderate ionic strengths, i.e. when the screening length is still not very large, and to behave more or less like a rigid rod. To evaluate the intrinsic viscosity of a rodlike polymer we have used the following formula given by Doi and Edwards [31]:

$$[\eta] = \frac{4\pi L^3 N_A}{90[\ln(L/d) - 0.8]M}, \tag{11}$$

where d is the diameter of the rod and L its length. Starting with the larger molecule, Na50PA48, the data given earlier lead to rigid-rod result $[\eta] = 1150$ cm^3 g^{-1}, which should be an upper limit for the intrinsic viscosity as κ^{-1} is increased. It has not reached even the lowest ionic strength measured, 2.0×10^{-4} M, but the decreasing slope of $[\eta]$ vs κ^{-1} at large κ^{-1} in Fig. 2, is probably a manifestation of an approach to this limit.

For Na50PA5, the rigid rod limit is 23 cm^3 g^{-1}. As can be seen in Fig. 3, this value is actually reached when $I = 8.0 \times 10^{-3}$ ($\kappa^{-1} = 34$ Å) and $[\eta]$ continues to increase with the increasing screening length. This behavior could be related to the interactions of the chain with the surrounding counterions (primary electroviscous effect). From this point of view, we should attribute the increase of intrinsic viscosity with κ^{-1} not only to the chain expansion due to the electrostatic repulsion, but also to an effective increase of the size due to the resistance to distortion of the surrounding ion atmosphere [4]. Probably there is also a contribution from the ordering of the water molecules in a solvation layer around the chain [49,50], where the water dipoles are oriented under the action of the electric field of the chain, which is characterized by an extremely high charge density. Fuoss and Strauss suggested increasing the effective hydrodynamic radius with a term proportional to κ^{-1}, treating the polyelectrolyte as a sphere [51]. Based on the description of the molecule as being rodlike, we propose the following relations:

$$d' = d + \kappa^{-1}/10, \tag{12}$$

$$L' = L + \kappa^{-1}/10 \tag{13}$$

for the calculation of the chain diameter and contour length, respectively. The factor 1/10 is purely empirical. Fuoss and Strauss needed at least four screening lengths to get in agreement with their data, although they had anticipated a factor less than 1. Wang has shown that the effective increase in the hydrodynamic volume is highly shear dependent [52]. By evaluating the intrinsic viscosity through Mooney's equation [53], Wang found that the increase in the apparent hydrodynamic radius for polystyrene latex particles was larger than κ^{-1} at shear rates less than 1000 s^{-1}, while at shear rates higher than this, the electroviscous contribution to the radius was smaller than the screening length and also proportional to it. Although the mechanism is more complicated than a simple hard-core interaction, this shows that the viscosity can be mapped onto such a behavior with κ^{-1} giving the ionic strength dependence at a given shear rate.

To be more specific, we should perhaps distinguish between at least two mechanisms, reflected by the two terms on the right-hand side of Eqs. (12) and (13). The solvation of the chain and the ions next to it would be expected to produce an almost constant hard core, represented by a shear plane close to the Stern layer or Outer Helmholtz Plane, a few Ångströms from the "molecular surface" [50]. This would remain in place even at high shear rates, whereas the perturbation of the diffuse double layer (primary electroviscous effect) would appear as a "soft" core, depending strongly on both κ^{-1} and the shear rate. In our empirical approach, we will use the same d and L for the "hard core" as before.

With Eqs. (12) and (13), Eq. (11) becomes a function of the ionic strength and $[\eta]$ increases beyond the original rigid-rod limit at low ionic strengths. For the lower molecular weight polyelectrolyte, Na50PA5, the point where the experimental data crosses over the predicted limit has now moved to the larger screening length of $\kappa^{-1} = 70$ Å. If we also use these equations for the low molecular weight poly(styrenesulfonate) sample ($M = 31\,000$) of Ref. [8], the extremely high intrinsic viscosity value, $[\eta] = 1050\ \mathrm{cm}^3\ \mathrm{g}^{-1}$, measured in the very low ionic strength region, can be obtained with $I = 4 \times 10^{-6}\ \mathrm{M}^7$.

The new, effective dimensions also affect the electrostatic persistence length, l_e, determined via Eq. (9). As shown in Fig. 4 we get lower values of l_e for Na50PA48 and in the range 3 Å $< \kappa^{-1} <$ 50 Å l_e varies as κ^{-1} instead of $\kappa^{-1.05}$, while for $\kappa^{-1} >$ 50 Å l_e tends to a plateau in accordance with theoretical predictions [15,24].

Although we are using Eq. (11) as if the molecules were fully extended, we do not expect them to become perfect rods, because the loss of chain entropy would be too great. It would in principle require an infinite force. Instead we would expect a chain to start approaching a maximum extension when κ^{-1} is of the same order as the size of the molecule, which could still be considered to be rodlike. Thus if the intrinsic viscosity was only a function of the dimensions of the polymer itself, the intrinsic viscosity of Na50PA5 should certainly have started to level off at the lowest ionic strengths in Fig. 3, where κ^{-1} is even approaching the contour length.

For the same reason, the persistence length is expected to reach a plateau as has been demonstrated by simulation [24] and is in fact also predicted by the full expression of the electrostatic persistence length in the OSF theory [15]. This is what we observe in Fig. 4 when we use the effective dimensions of Eqs. (12) and (13) to calculate the electrostatic persistence length for Na50PA48. It is possible to make a rough interpolation from the simulation results of chains with 320 and 1000 monomers and with a charge density similar to that of Na50PA48 (circa 580 monomers). This gives a deviation from the linear behavior around $\kappa^{-1} = 50$ Å which is in very good agreement with Fig. 4, particularly considering the approximate nature of the calculations. The effective dimensions thus lead to a reasonable result for the electrostatic persistence length.

4. Conclusions

In conclusion, we would like to point out the following observations regarding the behavior of 50% neutralized poly(acrylic acid) in aqueous solution from the measurements of viscosity at different ionic strengths by the isoionic dilution method:

1. At high ionic strength, $\kappa^{-1} <$ 3 Å, the electrostatic interactions are practically screened out and as a result the chain tends to behave as a neutral polymer. In the present case there is also a tendency towards ideal coil behavior as we are close to the Θ conditions for polyacrylate.
2. At lower ionic strength, $\kappa^{-1} >$ 3 Å, the polyelectrolyte chain is expanded towards a rodlike conformation and the maximum extension is most easily achieved by the lower molecular weight chain. This behavior is explained by the intra-chain electrostatic repulsions, which take effect just as the screening length becomes larger than the charge–charge separation.
3. At sufficiently low ionic strength, it seems that the counterions that are strongly correlated by the chain (primary electroviscous effect), and probably also the ordering of water dipoles due to the electric field, contribute to the viscosity through an effective increase of the hydrodynamic volume of the chain, which for a rodlike molecule would be most notable as an apparent increase of its diameter.
4. In addition at low ionic strength, considerable intermolecular electrostatic interactions appear, which are manifested through the very high values of the Huggins coefficient, K_H, compared to neutral polymers, and present a further dependence on the screening length, κ^{-1}. These interactions correspond to the secondary electroviscous effect.

Finally, we have to point out that both intra- and interchain electrostatic interactions contribute to the polyelectrolyte effect depending on the ionic strength of the solution. It seems that at higher ionic strength, when κ^{-1} is smaller than the chain dimensions, intramolecular repulsive electrostatic interactions prevail, while at lower ionic strength, where the screening length extends significantly beyond the chain, intermolecular electrostatic interactions constitute a major part.

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References

[1] Schmitz KS. Macroions in solution. Weinheim: VCH, 1993.
[2] Förster S, Schmidt M. Adv Polym Sci 1995;120:51.
[3] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1953. p. 629.
[4] Russel WB. J Fluid Mech 1978;85:209.
[5] Hess W, Klein R. Adv Phys 1983;32:173.
[6] Rabin Y. Phys Rev A 1987;35:3579.
[7] Cohen J, Priel Z, Rabin Y. J Chem Phys 1988;88:7111.
[8] Cohen J, Priel Z. Polym Commun 1989;30:223.
[9] Yamanaka J, Matsuoka H, Kitano H, Hasegawa M, Ise NJ. Am Chem Soc 1990;112:587.
[10] Yamanaka J, Matsuoka H, Kitano H, Ise N. J Colloid Interface Sci 1990;134:92.
[11] Yamanaka J, Matsuoka H, Kitano H, Ise N, Yamaguchi T, Saeki S, Tsubokawa M. Langmuir 1991;7:1928.
[12] Antonietti M, Briel A, Förster S. J Chem Phys 1996;105:7795.
[13] Reed WF. J Chem Phys 1994;101:2515.
[14] Kratky O, Porod G. Rec Trav Chim 1949;68:1106.
[15] Odijk T. J Polym Sci Polym Phys Ed 1977;15:477.
[16] Skolnick J, Fixman M. Macromolecules 1977;10:944.
[17] Maret G, Weill G. Biopolymers 1983;22:2727.
[18] Tricot M. Macromolecules 1984;17:1698.
[19] Ghosh S, Xiao L, Reed CE, Reed WF. Biopolymers 1990;30:1101.
[20] Reed WF, Ghosh S, Medjahdi G, Francois J. Macromolecules 1991;24:6189.
[21] Degiorgio V, Mantegazza F, Piazza R. Europhys Lett 1991;15:75.
[22] Micka U, Kremer K. Phys Rev E 1996;54:2653.
[23] Micka U, Kremer K. J Phys: Condens Matter 1996;8:9463.
[24] Ullner M, Jönsson B, Peterson C, Sommelius O, Söderberg B. J Chem Phys 1997;107:1279.
[25] Reed CE, Reed WF. J Chem Phys 1991;94:8479.
[26] Seidel C, Schlacken H, Müller I. Ber Bunsenges Phys Chem 1996;100:175.
[27] Pals DTF, Hermans J. J Rec Trav Chim 1952;71:433.
[28] Terayama H, Wall FT. J Polym Sci 1955;16:357.
[29] Yamakawa H, Fujii M. Macromolecules 1974;7:128.
[30] Kirkwood JG, Auer PL. J Chem Phys 1951;19:281.
[31] Doi M, Edwards SF. The theory of polymer dynamics. Oxford: Oxford University Press, 1988. p. 289.
[32] Takahashi A, Nagasawa N. J Am Chem Soc 1964;86:543.
[33] Manning GS. J Chem Phys 1969;51:924.
[34] Bokias G, Staikos G. Polymer 1995;36:2079.
[35] Moan M, Wolff C. Polymer 1975;16:776.
[36] Ullner M, Staikos G, Theodorou DN. Macromolecules 1998;31:7921.
[37] Davis RM, Russel WB. Macromolecules 1987;20:518.
[38] Russel WB. J Chem Soc Faraday Trans 2 1984;80:31.
[39] Sogami I, Ise N. J Chem Phys 1984;81:6320.
[40] Ise N. Angew Chem Int Ed Engl 1986;25:323.
[41] Overbeek JTG. J Chem Phys 1987;87:4406.
[42] Woodward CE. J Chem Phys 1988;89:5140.
[43] Okubo T. J Chem Phys 1987;86:5182.
[44] Okubo T. Acc Chem Res 1988;21:281.
[45] Guldbrand L, Jönsson B, Wennerström H, Linse P. J Chem Phys 1984;80:2221.
[46] Ise N, Okubo T. J Am Chem Soc 1968;90:4527.
[47] Tsuji T, Norisuye T, Fujita H. Polym J 1975;7:558.
[48] Muroga Y, Noda I, Nagasawa M. Macromolecules 1985;18:1576.
[49] Franks F. Water. London: The Royal Society of Chemistry, 1984.
[50] Hunter RJ. Zeta potential in colloid science. London: Academic Press, 1981.
[51] Fuoss RM, Strauss UP. Ann NY Acad Sci 1949;51:836.
[52] Wang YL. J Colloid Interface Sci 1970;32:633.
[53] Mooney M. J Colloid Sci 1951;6:162.