ciably from a rodlike shape. This is in agreement with what has been concluded from the salt dependence of the second virial coefficient determined by static light scattering.[19]

At low salt concentrations the intensity correlation functions contain a contribution of a slow mode that is probably due to the (time-dependent) formation of loose aggregates or local ordering on a short length scale.

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Viscosity of Dilute Polyelectrolyte Solutions: Concentration Dependence on Sodium Chloride, Magnesium Sulfate, and Lanthanum Nitrate

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ABSTRACT: The reduced viscosity of polyelectrolyte solutions has been measured by using fully sulfonated sodium-neutralized polystyrene to which magnesium sulfate or lanthanum nitrate has been added. The high accuracy and sensitivity of the experimental setup enables us to perform measurements at extremely low polymer and salt concentrations. It was found that increasing the charge of the cation from monovalent (Na^+) to divalent (Mg^{2+}) and trivalent (La^{3+}) shifts the maximum position of the reduced viscosity toward higher polymer concentrations and decreases the absolute value of the reduced viscosity. A good agreement between experimental findings and theoretical predictions was obtained.

Introduction

Early investigations of the anomalous viscosity of polyelectrolyte solutions without added salt appeared to suggest that the reduced viscosity would increase without bound as one lowers the polyion concentration.[1] However, a careful investigation of the dilute solution behavior revealed that the apparently unbounded rise of the reduced viscosity is always followed by a maximum and normal polymer behavior which is recovered at the extrapolated limit of zero polyelectrolyte concentration.[2] It has been argued that the observed behavior is a consequence of the screening of long-range intermolecular interactions by the residual electrolyte in the solution.[2] This explanation was supported by the observation of "regular" neutral polymer behavior upon isoionic dilution of polyelectrolyte solutions.[3,4] Most of the experimental work dealt with the existence of the maximum that appeared at relatively low polymer concentrations and therefore was close to the limit of the accuracy of the measuring systems. On the other hand, there are no systematic measurements, as far as we know, of a given polyelectrolyte vs chemical and physical parameters.

We have developed an apparatus that enables us to perform accurate measurements of the shear viscosity of low ionic strength, dilute polyelectrolyte solutions down to polymer concentrations below 1 part per million.[5,6] A

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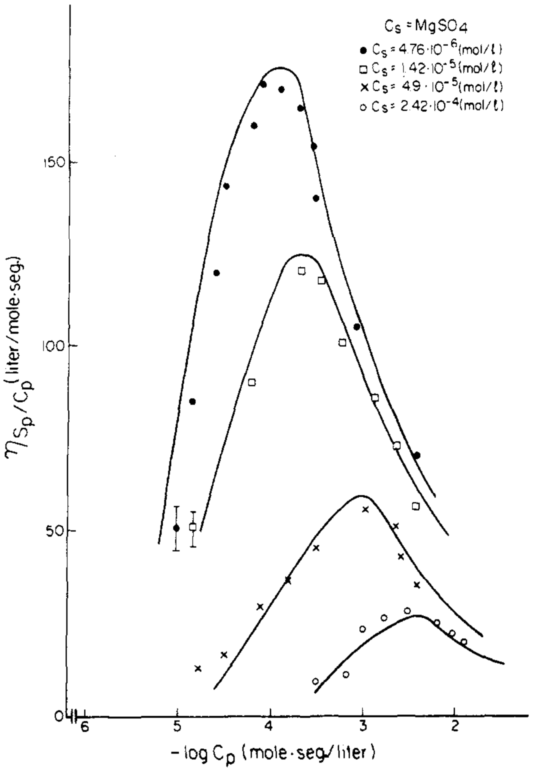

Figure 1. Reduced viscosity η_{Sp}/C_p vs log polymer concentration at four $MgSO_4$ concentrations. The molecular weight of the polyelectrolyte is 88 000 with a weight distribution of M_w/M_n = 1.0089. The points are experimental, and the curve reproduces the theoretical prediction.

theoretical expression for the viscosity of such solutions has been derived[7] by applying a mode–mode coupling approximation to the hydrodynamics of charged Brownian spheres.[8] Very good agreement between predicted and observed viscosity as a function of polymer and salt concentration and molecular weight is obtained in the low salt, dilute solution range.[7,9,10] Furthermore, it appears that the equation relating the viscosity to polymer and salt concentrations gives a qualitatively correct description of the viscosity of semidilute solutions, indicating that independent of polyion concentration, the hydrodynamics of low ionic strength polyelectrolyte solutions is dominated by electrostatic repulsion between polyions.

All the above work was done with monovalent added ions. The aim of this present contribution is to investigate the viscosity in the presence of different cations at extremely low polyelectrolyte and salt concentrations.

Materials and Methods

The polyelectrolyte used in the experiment was fully sulfonated sodium-neutralized polystyrene (Pressure Chemical Co., Pittsburgh, PA). These polymers are prepared by the "living polymer" polymerization method and possess a very sharp molecular weight distribution (M_w/M_n = 1.0089) for molecular weight of 88 000. All other materials were analytical grade. Doubly distilled water was further filtered through a Millipore cleaning device (pore size 0.22 μm) until the resistance was 18 MΩ/cm. All the solutions were prepared by weight, by using analytical balance with an accuracy of $\pm 1 \times 10^{-5}$ g.

The measuring system has been described in detail in ref 7. It consists of the following components: (1) automatic Ubbelohde viscometer with shear rate of 600 1/s; (2) thermostat with long-time stability of $\pm 1 \times 10^{-4}$ °C;[5] (3) electrooptical time-of-flow measuring system with absolute accuracy of $\pm 1 \times 10^{-4}$ s.[6]

Results

All the measurements in this study were performed on relatively low molecular weight (88 000) poly(styrene-sulfonate). The choice of added divalent or trivalent ion is quite limited in such studies due to precipitation of the polymer. It was found that Mg^{2+} and La^{3+} may be used as added divalent and trivalent ions, at least in the range of polymer and salt concentrations used in this work.

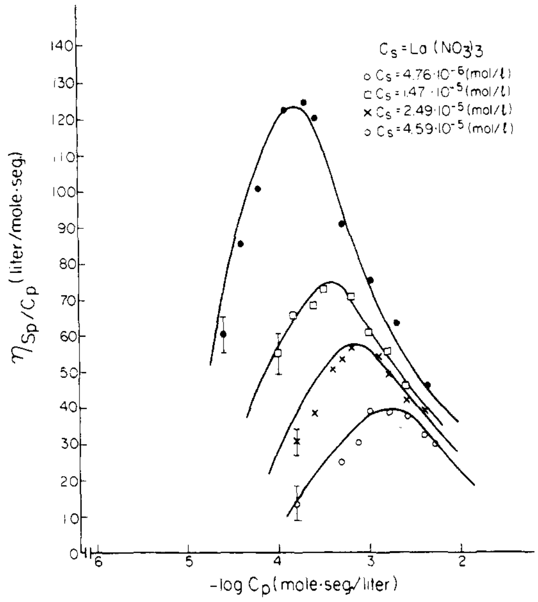

Figure 2. Reduced viscosity η_{Sp}/C_p vs log polymer concentration at four $La(NO_3)_3$ concentrations. The molecular weight of the polyelectrolyte is 88 000 with weight distribution of M_w/M_n = 1.0089. The points are experimental findings, and the curve reproduces the theoretical prediction.

Figure 1 shows a typical dependence of the reduced viscosity (η_{SP}/C_p) vs log polymer concentration (C_p) at different ionic strengths of $MgSO_4$. In the range 4.76×10^{-6}–2.92×10^{-4} M $MgSO_4$ concentration a familiar polyelectrolyte behavior is observed. Increasing the ionic strength decreases the absolute value of η_{SP}/C_p, and the maximum is shifted toward higher polymer concentrations. Similar behavior was obtained by using $La(NO_3)_3$ as an added salt (Figure 2). The comparison between the effects of the different salts (NaCl, $MgSO_4$, $La(NO_3)_3$) and η_{SP}/C_p vs log C_p behavior is represented in Figure 3. As can be seen the value of η_{SP}/C_p is reduced drastically (by a factor of ~4.5) when the added ion is changed from monovalent (NaCl) to divalent ($MgSO_4$). Further though less dramatic decrease is observed upon replacing the divalent ion by a trivalent one ($La(NO_3)_3$). Furthermore, the position of the maximum in η_{SP}/C_p is systematically shifted toward higher polymer concentrations as the charge of the counterions is increased. A linear relation between $(C_P/C_s)_{max}$ vs $2I/C_s$ (I is the ionic strength of the added salt) for the different salts measured is established (Figure 4).

Discussion

The viscosity of polyelectrolyte solutions originates in (a) the hydrodynamic contribution of the polymer and (b) the charge effect of the polyion. To bring out the latter effect (polyion), we have chosen to investigate the relatively low molecular weight polymers. Working with low molecular weight polyelectrolytes (16 000–345 000) decreases the net measured effect. However, the accuracy and sensitivity of our measuring system enable us to measure the resulting small differences in time of flow with high accuracy. The effect of the high rate of shear (600 s^{-1}) on polymer configuration and therefore on its viscosity, which is one of the main drawbacks of the capillary viscometers, is small when low molecular weight polyelectrolytes are studied.

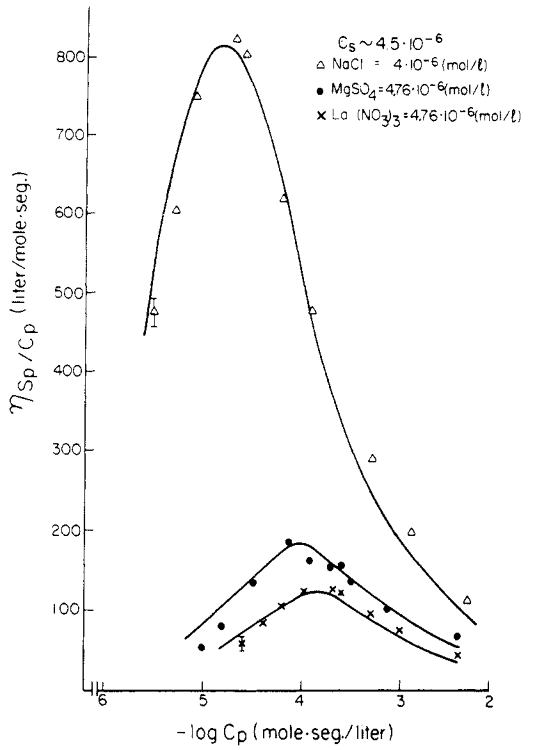

Figure 3. Reduced viscosity vs log polymer concentration for three different salts (NaCl, $MgSO_4$, $La(NO_3)_3$) at almost the same salt concentration. The points are experimental findings, and the curves are theoretical prediction.

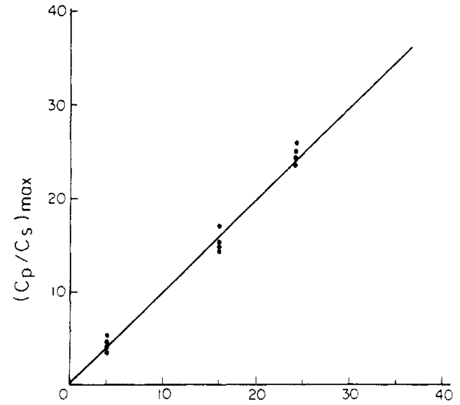

Figure 4. C_P/C_s at the maximum of the reduced viscosity vs $2I/C_s$ for all salts measured by us (NaCl, $MgSO_4$, $La(NO_3)_3$). The points are experimental findings, while the line is a theoretical prediction.

To describe the behavior of η_{SP}/C_P vs C_P of polyelectrolyte solution at low ionic strength, the following equation is used:[7]

$$\eta_{SP}/C_P \equiv \frac{\eta - \eta_0}{\eta_0 C_P} = AC_P/\kappa^3 \qquad (1)$$

where η_0 and η are respectively the solvent and solution viscosities, C_P is the monomer concentration of the polyelectrolyte, κ^{-1} is the Debye screening length defined by $\kappa^2 \sim C_P + \sum z_s^2 C_s$, where C_s and z_s are the concentration and valence of the added salt ion, and A is a numerical factor that is proportional to the product of the hydrodynamic radius of the macromolecule (R_H) and the square of Bjerium length ($l_B = \epsilon^2/\epsilon_0 k_B T$). Notice that the above expression contains a maximum of the reduced viscosity dependence on polymer concentration and that increasing the salt concentration (C_s) shifts the peak to higher polymer concentrations.

The experimental results agree with the theoretical curve to a constant factor as can be seen in Figures 1 and 2. The drawn curves are theoretical predictions, while the points are the experimental data. It was found that for a given ionic charge of added salt and molecular weight of the polymer, the numerical factor (A) is constant (independent of polymer and salt concentration) at least in the range of concentrations used (see Figures 1 and 2). This finding is in accord with the theoretical prediction.[7] However, we cannot use the same factor for the three added ions. The numerical factor (A) was found to be 6 for Na^+, 3.2 for Mg^{2+}, and 2.5 for La^{3+} (Figure 3). These factor differences can be qualitatively understood in terms of the ion condensation theory,[11] which predicts neutralization of macroions so that the net charge of particles decreases as condensation of small ions occurs. The condensation is more intensive as the charge of the small ions increases. This agrees with the results we have obtained. The charge of the polyion Z is one of the components of the numerical factor,[7] so as the charge of the small ions increases the above factor decreases. Further theoretical investigation, which is clearly needed, is beyond the scope of this work.

A linear relationship was obtained regardless of the nature of the different counterions $(C_P/C_s)_{max}$ and the $2I/C_s$ (Figure 4). These findings are in accord with the predictions of the proposed theory.[7]

To conclude, the qualitative behavior (the line shape) of the reduced viscosity vs polymer concentration in the extremely low concentration regime is the same for the three different counterions. Increasing the charge of the added ions from monovalent to divalent to trivalent reduces the η_{Sp}/C_p measured and shifts the positions of the maxima toward higher polymer concentrations. A good agreement between the theory[7] and the experimental results was obtained.

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