Electroviscous Effects of Dilute Sodium Poly(styrenesulfonate) Solutions in Simple Shear Flow

Li Jiang, Dahong Yang, and Shing Bor Chen*

Department of Chemical and Environmental Engineering, National University of Singapore, Singapore 117576

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ABSTRACT: Electroviscous effects of dilute sodium poly(styrenesulfonate) solutions subject to a simple shear flow are studied experimentally. Emphasis is placed on investigation of the coupled primary and tertiary effects using different added salt species. At constant shear rate, the intrinsic viscosity is found to be in descending order for solutions with added LiCl, NaCl, and KCl at equal molar concentration. A similar descending order is also observed for $MgCl_2$, $CaCl_2$, and $BaCl_2$. The noticeable difference in the intrinsic viscosity between various added salts indicates that the primary effect associated with distortion of the electric double layer caused by the imposed flow cannot be neglected. The experimental data also show that the intrinsic viscosity of a solution with added divalent cations is lower than that with monovalent ones at constant ionic strength.

1. Introduction

Polyelectrolytes are polymers carrying charges due to dissociation of their ionizable groups in an aqueous solution and have been widely used in paints, cosmetics, and film industries.[1] Different from neutral polymers, polyelectrolytes have a comparatively extended conformation, owing to the repulsive intrachain electrostatic interaction screened by the surrounding small ions in the solution. As a result, their rheological properties in a dilute solution due to an applied flow will change accordingly. This is called a tertiary electroviscous effect. In addition, the imposed flow distorts the ionic cloud around each polyelectrolyte from its equilibrium state, leading to two effects. First, it results in additional energy dissipation associated with the electrical interaction between each polyelectrolyte and small ions. This direct effect, depending on the chain configuration, is analogous to the primary electroviscous effect of charged rigid spheres,[2] rods,[3] or polyions of arbitrary shape[4] but has sometimes been ignored in the field of flexible polyelectrolyte rheology. Second, an indirect effect changes the polyelectrolyte conformation through the modification of the intrachain electrostatic interaction, compared to that with equilibrium double layer. Therefore, the primary and tertiary effects are indeed coupled for polyelectrolytes. The objective of this paper is to conduct experiments to investigate these coupled effects.

Polyelectrolyte solutions can generally be categorized in two types: salt-free solutions and solutions with added salt. For a moderately dilute salt-free solution, the empirical Fuoss law is commonly used

$$\eta_{\mathrm{red}} = \frac{\eta - \eta_{\mathrm{s}}}{\eta_{\mathrm{s}} C} = \frac{A}{1 + BC^{1/2}} \tag{1}$$

where η is the apparent viscosity of the solution, η_s is the solvent viscosity, C is the polyelectrolyte concentration, and A and B are constants. The Fuoss law states that the reduced viscosity decreases with increasing polyelectrolyte concentration. This prediction contradicts with the experimental observations for polyelectrolyte at sufficiently low concentration. It was found[5−7] that, upon increasing dilution of flexible polyelectrolytes at low ionic strength, the reduced viscosity may increase first, reach a maximum, and then decrease. Since a similar behavior can also be observed even for solutions of polyelectrolyte latices at low salt concentration,[8] the primary electroviscous effect was thought as a possible explanation for the maximum, as opposed to conformation change.

For a dilute solution with sufficient added salt, the reduced viscosity can be described by the Huggins relation

$$\eta_{\mathrm{red}} = [\eta] + k_{\mathrm{H}}[\eta]^2 C + O(C^2) \tag{2}$$

where $[\eta]$ is the intrinsic viscosity and k_H is the Huggins coefficient. This expression, based on a truncated virial expansion, becomes inaccurate when the polyelectrolyte concentration is sufficiently high. For polyelectrolyte solutions with added salt, prior experimental studies[9−11] found that the intrinsic viscosity decreases with increasing salt concentration. This can be explained by the tertiary electroviscous effect. As more salts are added, the intrachain electrostatic repulsion is weakened by the stronger screening effect of small ions. As a result, the polyelectrolytes are more compact and flexible, leading to a smaller resistance to fluid flow and thus a lower viscosity. Davis and Russel[12] modified a wormlike-chain model by incorporating the tertiary effect on the chain conformation to predict the intrinsic viscosity in zero-shear limit. The effect of the intrachain electrostatic repulsion on the chain conformation is obtained based on the equilibrium interaction, which depends on the Debye screening length,

$$\lambda = \left(\frac{\epsilon k_{\mathrm{B}} T}{e^2 \sum_i c_i z_i^2} \right)^{1/2} \tag{3}$$

where ϵ is the permittivity of the solution, k_BT is the thermal energy, e is the elementary charge, and c_i and

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* Corresponding author: E-mail checsb@nus.edu.sg.

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z_i are the molar concentration and valence of the ions of species *i*. Note that when the concentration of added salt is very low, eq 3 needs to be modified by including the charge contribution of the dissociating counterions from the polyelectrolytes. Because the equilibrium interaction is used, their theory predicts that the intrinsic viscosity is independent of ion species at constant ionic strength. At very high ionic strength, the intrachain electrostatic interaction is nearly screened out, and the chains behave as neutral polymers. Aside from the tertiary effect, the intrinsic viscosity will indeed be affected by the ionic cloud distortion and thus cannot be accurately predicted by their theory.

The effects of ion valence and polyelectrolyte charge density have also been examined. Cohen and Priel[13] conducted experiments at very low ionic strength and found that when the counterion valence of added salt changes from monovalent (NaCl) to divalent ($MgSO_4$), the reduced viscosity decreases by a factor of about 4.5. If $La(NO_3)_3$ is used, the reduced viscosity will be further decreased although not drastically. As for polyelectrolyte charge density, the intrinsic viscosity was found to increase with it because of an enhanced intrachain electrostatic repulsion.[14]

We recently developed a charged FENE dumbbell model to investigate the rheological behavior of a dilute solution of flexible polyelectrolytes subject to an extensional flow.[15] This is the first theoretical work to formulate the coupled primary and tertiary effects in the literature. We found that, apart from the additional energy dissipation due to the primary effect, the double-layer deformation leads to a stronger intrachain repulsion on average than in equilibrium. The extent of ionic cloud distortion can be characterized by the ion Peclet number defined as $Pe = \dot{\gamma}\lambda R_m/D$, where $\dot{\gamma}$ is the characteristic value of velocity gradient, D is the diffusion coefficient of the small ions (assumed to be identical in our theory), $R_m = \langle R^2\rangle^{1/2}$ is the root-mean-square end-to-end distance of the dumbbell. Besides, the theoretical predictions show that the extensional viscosity increases with decreasing ion diffusivity at constant flow strength and ionic strength. This finding suggests experimental investigations using ions of equal valence but different mobility. Lapanje and Kovac[16] measured the intrinsic viscosity of a NaPSS solution with added NaCl, which was found different from that of a KPSS solution with added KCl at the same concentration. However, this difference was not examined systematically and thoroughly in their work. In the present study, we will conduct experiments using different ion species to investigate the electroviscous effects of a dilute polyelectrolyte solution under shear flow.

2. Experiments

The polyelectrolyte used is analytic grade poly(sodium 4-styrenesulfonate) (NaPSS) purchased from Aldrich Chemical Inc. (Milwaukee, WI, catalog no. 43457-4). NaPSS is a flexible, negatively charged polyion when dissolving in water. The average molecular weight is $M_w = 10^6$ g/mol according to the manufacturer's analysis. Deionized water from an ultrapure water generator was used in the preparation of NaPSS solutions. The conductivity of the deionized water was measured with a conductivity meter (Denver Instrument model 20) and was found to be lower than 1.0 μS/cm. All salts used in the experiments are of analytical grade, including LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$, and $BaCl_2$ purchased from Merck kGaA, BDH Laboratory Supplies, and Hayashi Pure Chemical Industries.

NaPSS solutions were prepared by adding a precise amount of NaPSS powder to the deionized water and then stirring the mixture thoroughly using a magnetic stirrer until all the NaPSS powder had dissolved into the water. For solutions with external salt, we simply added the salt of correct mass to attain a desired molar concentration.

The radius of gyration of NaPSS was measured with static light scattering using a Brookhaven BI-9000AT digital autocorrelator and an EMT9865 goniometer. The apparent viscosity of the NaPSS solution was measured using a Haake RS75 rheometer with a DC50 temperature controller (water circulating bath). The measurement unit is directly connected to a computer with a software installed, which can control the stress and shear rate as well as process the data. The drive shaft is centered by an air bearing which ensures an almost frictionless transmission of the applied stress to the test sample. A double-gap cylinder sensor (DG41) was used because of low apparent viscosity of dilute NaPSS solutions. The double shearing surfaces of this particular system result in a higher shear stress than what is customary for a comparable concentric cylinder system. The measurement validity of this sensor is for shear rate ranging from 100 to 1000 s^{-1}. All measurements were conducted with sample temperature maintained at 25.0 °C. A controlled-strain-rate mode was used to measure the stress of a NaPSS solution of 6.3 cm^3 at various shear rates, and the apparent viscosity can then be determined.

3. Results and Discussion

As mentioned in the Introduction, the main concern of this paper is to study the coupled primary and tertiary effects for a polyelectrolyte solution with sufficient added salt. We first examine the flow properties of polyelectrolyte solutions with different added salts—LiCl, NaCl, and KCl in simple shear flow. Since these salts are all chlorides of group I metals, the three cations have an equal valence and similar chemical properties. In our experiments, the concentration of added monovalent salt ranges from 0.0005 to 0.01 M and is sufficiently high to give a screening effect. At salt concentration of 0.0005 M, the measured radius of gyration of NaPSS by static light scattering is about 40 nm, and thereby the corresponding overlap concentration is estimated to be 6.3×10^{-6} M (6.3 g/L). As salt concentration increases, the enhanced screening effect causes the radius of gyration to decrease, thereby leading to an increase in the overlap concentration. To ensure dilute solutions in our experiments, the concentrations of NaPSS are all lower than 6.3 g/L. In fact, we have examined the experimental data to find that the polyelectrolyte concentrations in our samples are all lower than that for the maximum reduced viscosity. Figure 1 presents the apparent viscosity of 0.4 g/L NaPSS as a function of shear rate at various concentrations of added LiCl, NaCl, and KCl. The results for a solution without external salt are also shown for comparison. It can be seen that all NaPSS solutions are shear thinned, and the apparent viscosity decreases with increasing salt concentration.

Figure 2 plots the reduced viscosity against the NaPSS concentration with added LiCl of various concentrations at shear rate of 1000 s^{-1}. Note that, instead of conducting an isoionic dilution, we prepared the NaPSS solutions of various concentrations at constant added salt concentration. It can be seen that the reduced viscosity is a linear function of the NaPSS concentration. A similar behavior can be found for NaCl and KCl as shown in Figure 3 for salt concentration of 0.002 M. Such linear dependence on NaPSS concentration was also observed for other shear rate values in our experi-

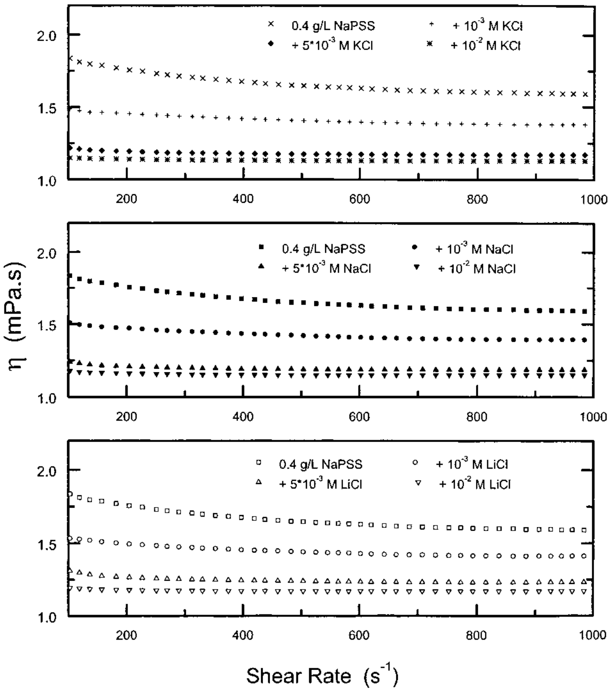

Figure 1. Shear rate dependence of apparent viscosity of 0.4 g/L NaPSS solutions with various concentrations of added LiCl, NaCl, and KCl.

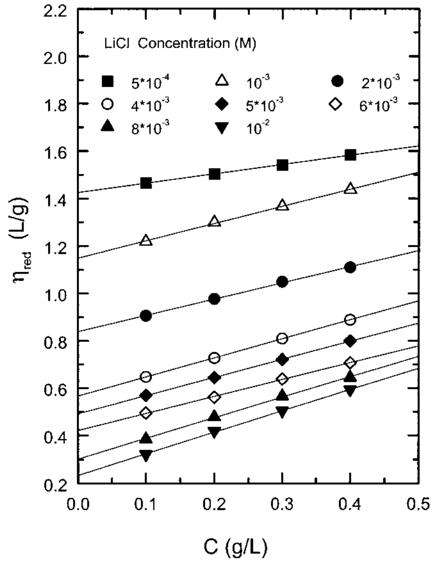

Figure 2. Variation of reduced viscosity with NaPSS concentration for solutions with added LiCl at $\dot{\gamma} = 1000$ s^{-1}.

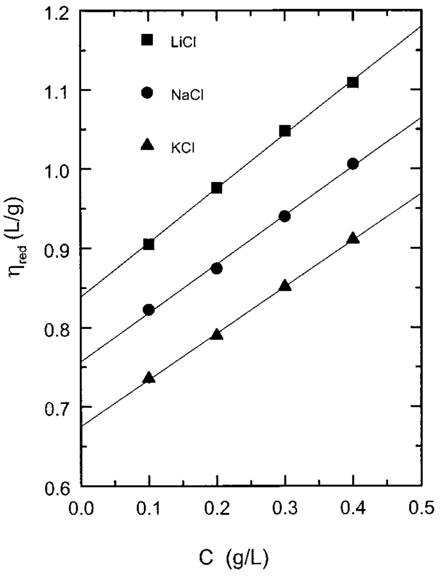

Figure 3. Variation of reduced viscosity with NaPSS concentration for various added salts of 0.002 M at $\dot{\gamma} = 1000$ s^{-1}.

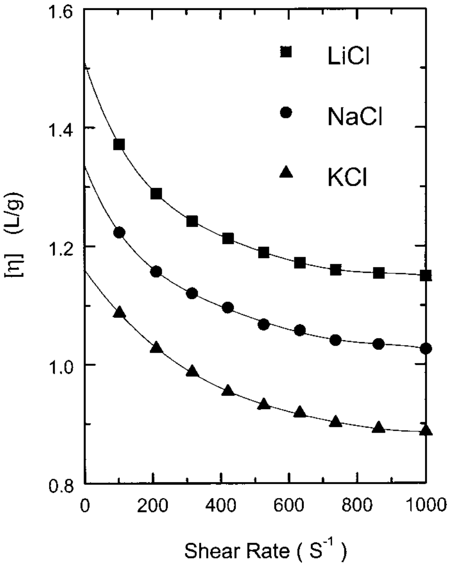

Figure 4. Shear rate dependence of intrinsic viscosity of NaPSS solution with various added salts at 0.001 M.

ments. To extract the behavior of polyelectrolytes in infinite dilution where the interchain interactions are all negligible, we fit the data with the Huggins relation (2) to obtain the intrinsic viscosity and the Huggins coefficient. It has been pointed out that the measurement of intrinsic viscosity is not affected by the dilution method, as opposed to the Huggins coefficient.[9] Pals and Hermans[17] have found that the Huggins coefficient determined by the isoionic dilution method is larger than that by the method of constant added salt concentration. In Figure 2, the line slope associated with the Huggins coefficient becomes smaller for lower salt concentration. As just mentioned, our samples were prepared by fixing the added salt concentration, so the overall ionic strength increases with increasing NaPSS concentration due to the dissociation of the ionizable groups. Since the polyelectrolyte contribution to the ionic strength becomes progressively important as the added salt concentration decreases, it leads to a stronger screening and may therefore account for the reduction in the slope mainly via the weakened secondary and tertiary effects for the cases at low salt concentration.

To examine the effect of different ion species, we present the variation of intrinsic viscosity with shear rate for three monovalent salts at 0.001 M in Figure 4. As expected, flexible polyelectrolyte solutions in infinite dilution are shear thinned. This is due to the fact that as the flow strength increases, the chains are progressively stretched and increasingly oriented with the flow direction, thereby exhibiting a shear thinning behavior. It can also be found that the intrinsic viscosity is LiCl > NaCl > KCl for all values of shear rate. This observation cannot be elucidated by the conventional tertiary electroviscous effect associated with the conformation change due to the electrostatic interaction. Previous studies on zero-shear intrinsic viscosity[9,12] used an equilibrium intrachain electrostatic interaction that is a function of the double-layer thickness (or the ionic strength). Such a model would predict an equal zero-shear intrinsic viscosity for the three salts of equal molar concentration. Because of the constraint of our rheometer, we were unable to obtain reliable viscosity for shear rate lower than 100 s^{-1}. Nonetheless, we still extrapolate the data in Figure 4 to get rough estimates of the zero-shear intrinsic viscosity, which show the same order for the three salts. A similar observation for zero-shear intrinsic viscosity was reported by Lapanje and Kovac[16] using KPSS in KCl and NaPSS in NaCl.

Recently, we developed a charged FENE dumbbell model to investigate the flow behavior of a dilute solution of flexible polyelectrolytes in extensional flow.[15] The double-layer deformation caused by the flow is taken into account. We find that the double-layer distortion gives rise to additional energy dissipation (primary effect) as well as increased chain extension on average. The latter can be regarded as a correction to the tertiary effect with negligence of the double-layer deformation. In the present study, the applied simple shear flow consists of a straining and a rotational part. The rotational flow drives the small ions to rotate with the polyelectrolyte at equal angular velocity and therefore does not give rise to any deformation of the ionic cloud.[2,3] Nonetheless, this flow component does affect the configuration distribution of the polyelectrolytes. The straining flow, as just mentioned, distorts the double layer, leading to additional energy dissipation. Besides, the deformed ionic cloud will modify the polyelectrolyte conformation. We are unable to calculate the average conformation change because the configuration distribution affected also by the rotational part is not yet available. But we speculate that in simple shear flow the double-layer deformation still enhances the stretching of polyelectrolytes on average, leading to higher stiffness and hence an increase in the apparent viscosity. Both effects become stronger as the ionic cloud is more deformed, i.e., larger ion Peclet number. Since the two effects both depend linearly on the flow strength for weak flows, a constant contribution to the intrinsic viscosity at low shear rates will result, depending on the ion diffusivity. A similar behavior has also been predicted for a dilute solution of charged rigid rods,[3] despite the absence of conformation change.

To compare the diffusivities of three cations, we measured the conductivity of the aqueous solutions for each salt up to 0.01 M to find that the conductivity increases linearly with salt concentration. Such results indicate that the molar conductivity remains constant in infinite dilution limit. Since the molar conductivity in this limit is a linear combination of the cation and anion mobilities, the cation mobility is found to be $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ from our measurements, in agreement with the data in the literature.[19] Therefore, the extent of double-layer distortion at constant shear rate is KCl < NaCl < LiCl. It has been seen from Figure 4 that at constant shear rate the intrinsic viscosity is in descending order for LiCl, NaCl, and KCl at equal molar concentration (equal ionic strength). This experimental observation is in qualitative agreement with the tendency deduced from our theoretical model. It is worth noting that in Figure 4 the difference in intrinsic viscosity between any two salt species at a given shear rate is accounted for only by the effect of ion cloud distortion and should be in proportion to the difference in the inverse cation diffusivity, according to our model. Examining the results in the figure finds that the proportionality constant, which in general depends on the double-layer thickness, appears to be nearly independent of the flow strength in our shear rate range. This behavior is similar to the shear rate independent primary effect of charged rigid spheres as long as the double-layer distortion remains weak[20] but differs from the shear thinned distortion effect of charged rods[3] at sufficiently high shear rates. A comparison with the difference in the zero-shear limit seems to imply a possible shear thinning behavior for $\dot{\gamma} < 100$ s^{-1}, even though the zero-shear intrinsic viscosity by extrapolation of our data may not be accurate. Therefore, experimental measurements of viscosity for $\dot{\gamma} < 100$ s^{-1} are necessary to verify whether the distortion effect remains shear rate independent for weaker flows.

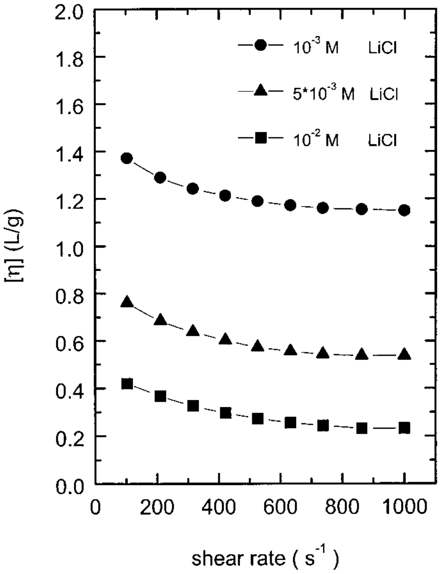

Figure 5. Shear rate dependence of intrinsic viscosity of NaPSS solution with added LiCl at various concentrations.

To investigate the salt concentration dependence, we plot in Figure 5 the intrinsic viscosity vs shear rate for the case with added LiCl at various concentrations. It can be seen that the intrinsic viscosity increases with decreasing concentration of added salt. With more added salt, i.e., stronger screening effect, the polyelectrolytes become more compact and possess higher flexibility (more like neutral polymers), leading to a smaller resistance to the fluid flow. It can be seen from Figures 4 and 5 that the trend of intrinsic viscosity with respect to the salt species or concentration is unchanged by varying the shear rate. Therefore, we will choose the data at shear rate of 1000 s^{-1} to make more discussion.

The results of intrinsic viscosity are plotted against the added salt concentration at shear rate of 1000 s^{-1} in Figure 6. Before analyzing the data, we would like to point out that at the salt concentrations in our experiments not all ionizable groups on a NaPSS chain can dissociate because the distance between two neighboring groups (=0.252 nm) is shorter than the Bjerrum length ($L_B = 0.7$ nm at 25 °C). For such a case, Manning proposed a counterion condensation theory,[18] stating that a polyelectrolyte chain behaves as one with constant effective charge density e/L_B, and the Debye–Huckel approximation is valid for mobile ions. To the contrary, Davis and Russel[12] numerically solved the nonlinear Poisson–Boltzmann equation for symmetric

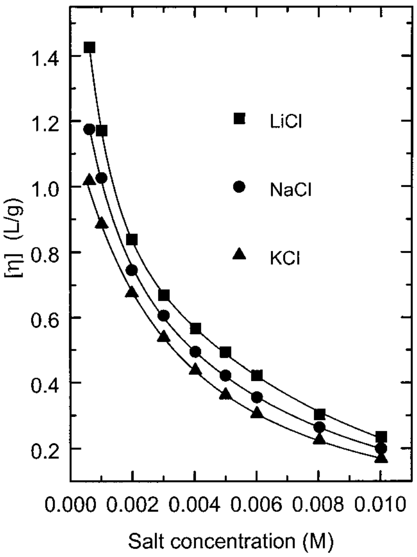

Figure 6. Variation of intrinsic viscosity of NaPSS solution with salt concentration at $\dot{\gamma} = 1000$ s^{-1}.

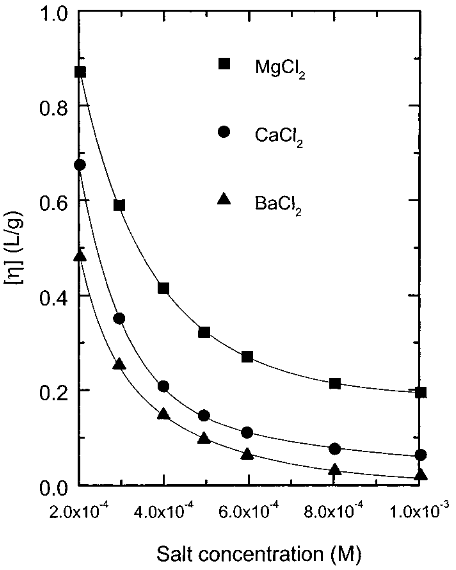

Figure 7. Variation of intrinsic viscosity of NaPSS solution with salt concentration at $\dot{\gamma} = 1000$ s^{-1}.

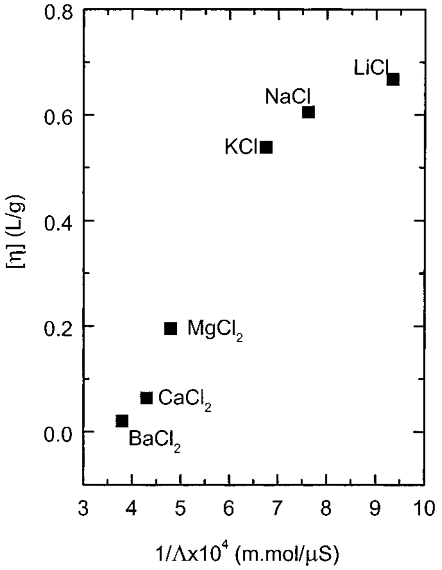

Figure 8. Intrinsic viscosity vs inverse molar conductivity for various added salts at equal ionic strength for $\dot{\gamma} = 1000$ s^{-1}. The salt concentrations are 0.001 and 0.003 M for the divalent and monovalent cations, respectively.

electrolyte to find that the effective charge density of a chain decreases with decreasing ionic strength. In our experiments, a/λ ranges from 0.036 to 0.17 with $a = 0.5$ nm being the backbone radius, so the effective charge density was estimated to vary from $0.9e/L_B$ to $1.2e/L_B$, using Davis and Russel's figure.[9] While the effective charge density decreases slightly with decreasing salt concentration, the intrinsic viscosity still increases as shown in Figure 6. This can be explained by the strengthened primary and tertiary effects when the ionic strength is reduced. However, the former was ignored in most studies on flexible polyelectrolytes. It can also be seen from the figure that the difference in intrinsic viscosity between two different salt species increases with decreasing ionic strength, indicating an enhanced distortion effect by reducing the salt concentration.

To confirm our intriguing findings using monovalent salts, we also conducted similar experiments using different divalent cations—$BaCl_2$, $CaCl_2$, and $MgCl_2$. The salt concentration ranges from 0.0002 to 0.001 M, such that all NaPSS solutions are in dilute regime. The mobility is found to be $Ba^{2+} > Ca^{2+} > Mg^{2+}$ as determined by the conductivity measurements. Figure 7 presents the intrinsic viscosity as a function of the salt concentration at shear rate of 1000 s^{-1}. Analogous to the case of monovalent cations, the intrinsic viscosity increases with decreasing ion diffusivity.

It is interesting to compare the effect of double-layer deformation for different cation valences. A comparison between the results in Figures 6 and 7 finds that the at salt concentration of 0.001 M the intrinsic viscosity is much lower for divalent cations than for monovalent ones. This behavior is similar to what was observed by Cohen and Priel,[13] even though the ionic strength in their experiments is much lower. To analyze the data in a more meaningful way, we choose the data for monovalent cations at 0.003 M and for divalent cations at 0.001 M, so that the ionic strength is identical, implying an equal tertiary effect when the double-layer deformation is ignored. Such a comparison enables us to isolate the effect associated with the ionic cloud distortion for these two types of salts. We find that the intrinsic viscosity has the order LiCl > NaCl > KCl > $MgCl_2 > CaCl_2 > BaCl_2$, while the salt molar conductivity has the opposite order. Figure 8 plots the intrinsic viscosity against the reciprocal of molar conductivity for these salts. This finding suggests a certain correlation between the electroviscous effect and the salt molar conductivity, which depends not only on the ion mobilities but also on their valences. In our theory,[15] the assumption of equal diffusivity for the cations and anions leads to the predicted effect of double-layer deformation that is independent of the ion valences. Unfortunately, our model is incapable of justifying the observations of smaller intrinsic viscosity for divalent cations, because the cation diffusivity is $K^+ > Na^+ > Li^+ > Ba^{2+} > Ca^{2+} > Mg^{2+}$ reported in the literature.[19] The above analyses imply that ion valences may play an essential role in the effect of double-layer distortion. For a dilute suspension of charged spheres, Watterson and White[20] conducted a numerical investigation on the primary electroviscous effect with ion valence taken into account. In Figure 4 of their paper, it was predicted that the apparent viscosity of a suspension with added $LaCl_3$ is lower than that with added KCl at constant ionic strength. This result supports our argument. The other possible reason is that the ion condensation becomes more intensive for divalent cations,[13] leading to a lower effective charge density of the polymer chain and thus more compact conformation. To better understand and explain our experimental observations for polyelectrolytes, it is necessary to develop a theoretical model that takes into account ion valences as well as electrostatic nonlinearity in the double layer around the backbone.

4. Conclusions

The rheological behavior of dilute sodium poly(styrenesulfonate) solutions in simple shear flow has been studied experimentally using a Haake RS75 rheometer. Studies were focused on the coupled primary and tertiary electroviscous effects using different added salts. As expected, the addition of salt decreases the apparent viscosity of NaPSS solutions because of a strengthened screening effect and hence a weakened chain stiffness. The intrinsic viscosity of the solution has the order $K^+ < Na^+ < Li^+$ for monovalent cations and $Ba^{2+} < Ca^{2+} < Mg^{2+}$ for divalent cations at equal molar concentration. The difference in intrinsic viscosity for different salt species cannot be explained by the tertiary effect based simply on the equilibrium electrostatic interaction. One must take into account the distortion of the ionic cloud caused by the imposed flow. The experimental results agree qualitatively with the tendency deduced from our theory that, for fixed ion valence, a solution with added ions of larger diffusivity has a lower intrinsic viscosity. However, our model is incapable of giving an explanation for the observation that at constant ionic strength the intrinsic viscosity is smaller for the divalent cations than for the monovalent ones. It appears that ion valences and electrostatic nonlinearity play an important role in the effect of ionic cloud distortion. Finally, it is encouraged to conduct experiments at lower shear rates in order to obtain a more accurate zero-shear intrinsic viscosity for different added salt and examine the shear rate dependence of the distortion effect.

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References and Notes

(1) Dautzenberg, H.; Jaeger, W.; Kotz, J.; Philipp, B.; Seidel, Ch.; Stscherbina, D. *Polyelectrolytes: Formation, Characterization and Application*; Hanser: Munich, 1994.
(2) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge University Press: Cambridge, 1989.
(3) Chen, S. B.; Koch, D. L. *Phys. Fluids* **1996**, *8*, 2792.
(4) Allison, S. A. *Macromolecules* **1998**, *31*, 4464.
(5) Yamanaka, J.; Araie, H.; Matsuoka, H.; Kitano, H.; Ise, N.; Yamaguchi, T.; Saeki, S.; Tsubokawa, M. *Macromolecules* **1991**, *24*, 6156.
(6) Vink, H. *Polymer* **1992**, *33*, 3711.
(7) Ganter, J. L. M. S.; Milas, M.; Rinaudo, M. *Polymer* **1992**, *33*, 113.
(8) Yamanaka, J.; Matsuoka, H.; Kitano, H.; Ise, N. *J. Colloid Interface Sci.* **1990**, *134*, 92.
(9) Davis, R. M.; Russel, W. B. *Macromolecules* **1987**, *20*, 518.
(10) Bokias, G.; Staikos, G. *Polymer* **1995**, *36*, 2079.
(11) Roure, I.; Rinaudo, M.; Milas, M.; Frollini, E. *Polymer* **1998**, *39*, 5441.
(12) Davis, R. M.; Russel, W. B. *J. Polym. Sci., Part B* **1986**, *24*, 511.
(13) Cohen, J.; Priel, Z. *Macromolecules* **1989**, *22*, 2356.
(14) Kowblansky, M.; Zema, P. *Macromolecules* **1981**, *14*, 1451.
(15) Jiang, L.; Chen, S. B. *J. Non-Newtonian Fluid Mech.* **2001**, *96*, 445.
(16) Lapanje, S.; Kovac, S. *J. Macromol. Sci. Chem. A* **1967**, *1*, 707.
(17) Pals, D. T. F.; Hermans, J. J. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 433.
(18) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(19) Rieger, P. H. *Electrochmistry*; Prentice Hall: New York, 1987.
(20) Watterson, I. G.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1115.

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