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Boundary Element Modeling of the Primary Electroviscous Effect of Dilute Sodium Poly(styrenesulfonate) in Monovalent Salt Solutions

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The purpose of this note is to call attention to what we believe is a clear and convincing demonstration of the primary electroviscous effect in macromolecular transport. It is based on recent viscosity measurements of sodium poly(styrenesulfonate), PSS, solutions in the limit of low polymer concentration and low but finite shear rate reported by Jiang, Yang, and Chen.[1] At the same ionic strength of 0.003 M, the intrinsic viscosities of PSS in alkali chloride salt solutions are not the same but decrease in the order LiCl, NaCl, and KCl. Now PSS is a highly charged polyanion, and its global conformation is expected to be strongly ionic strength dependent due to the polymer's flexibility and the screening of backbone charges by counterions. This charge screening and concomitant conformational change influences the intrinsic viscosity of the polymer[2] and gives rise to what is known as the tertiary electroviscous effect. However, for monovalent alkali metal counterions at the same concentration, we can expect the extent of charge screening (and hence global conformation) to be similar in LiCl, NaCl, and KCl solutions, and hence, the tertiary electroviscous effects are expected to be the same in all three solutions. Rather than a *tertiary* electroviscous effect, the experimental trends are consistent with the *primary* electroviscous effect.[3−5] The physical basis of the primary electroviscous effect is the additional energy dissipation that is involved in distorting the ion atmosphere around a rigid polyion that is placed in a viscous shear field. It is a complex phenomenon[3−5] that depends on many factors, but for systems that are identical in every respect except for the mobility of counterion, the primary electroviscous effect decreases as the counterion mobility increases. This is just the trend seen experimentally since the limiting molar conductivities of the counterions increase on going from Li^+ to Na^+ to K^+. Jiang et al.[1] concluded, and we believe correctly, that the differences in the intrinsic viscosities are due to the primary electroviscous effect. The purpose of this note is to strengthen that conclusion by carrying out modeling studies using a boundary element procedure that calculates the primary electroviscous effect by numerically solving the various transport equations for rigid model polyions.[5] Basically, we would like to show that the experimental trend in the intrinsic viscosities is not only *qualitatively* consistent with the primary electroviscous effect but that trend is *quantitatively* consistent as well.

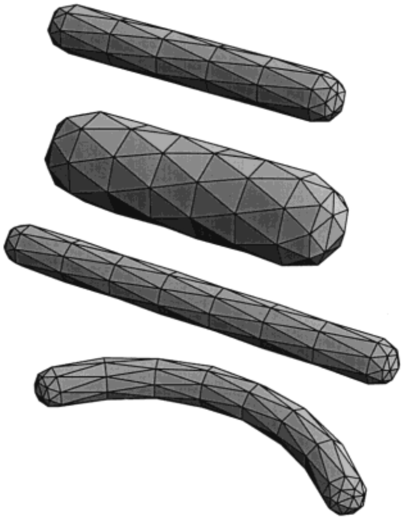

Figure 1. Surface structures used in BE modeling. From top to bottom, the structures consist of 144, 144, 176, and 176 plates; 20, 20, 30, and 30 equivalent charges; $a = 0.5$, 1.0, 0.5, and 0.5 nm, respectively. The lowest structure is bent to account for the effect of polyion curvature.

The boundary element (BE) methodology as applied to the electroviscous effect has been described in detail previously[5] so the present discussion shall be kept to a minimum. It can be applied to a rigid model macromolecule of arbitrary shape containing an arbitrary charge distribution within. The macromolecular surface is modeled as a rigid array of triangular plates, and Figure 1 illustrates a few examples. The fluid surrounding the model structure is divided into a series of shells that increase in thickness moving outward into the solution. The model structure is placed in one of five elementary shear fields, and the coupled continuum equations (low Reynolds number Navier−Stokes, solvent incompressibility, Poisson, and ion transport) are solved iteratively until the fields, forces, stresses, etc., converge. In the present work, 25 iterations are carried out for each elementary shear configuration. Suitable averaging over the excess stresses in these elementary shear configurations then gives the shape factor, ξ, or Simha coefficient (see, for example, ref 6). This is a dimensionless quantity that equals 2.5 for an uncharged sphere but is greater than 2.5 for uncharged nonspherical particles. It is closely related to the intrinsic viscosity in the limit of zero shear, $[\eta]$,

$$[\eta] = \frac{N_{\mathrm{av}} V_{\mathrm{p}}}{M}\,\xi \tag{1}$$

where N_{av} is Avogadro's Number, V_{p} is the volume of the model macromolecule, and M is its molecular weight. In the present work, we shall be primarily interested in the intrinsic viscosity *ratio* of the same macromolecule in different solvents which do not alter its conformation and so

$$X(2,1) \equiv \frac{[\eta(2)]}{[\eta(1)]} = \frac{\xi(2)}{\xi(1)} \tag{2}$$

where "1" and "2" denote different solvent conditions. In the present work, the solvent contains 0.003 M monovalent salt at 25 °C, where "1" corresponds to NaCl

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Table 1. Boundary Element Model Results

model	n	linear/bent	a (nm)	ξ_0	ξ(LiCl)	ξ(NaCl)	ξ(KCl)
I	20	linear	0.5	7.64	17.45	15.74	13.90
II	20	linear	1.0	4.08	6.53	6.10	5.64
III	30	linear	0.5	12.36	24.49	22.36	20.04
IV	30	bent	0.5	5.87	11.76	10.72	9.60

and "2" to LiCl or KCl. Equation 2 provides the direct link between theory/modeling and experiment.

There is a difficulty in modeling PSS in the present application since with a molecular weight of 1 × 10^6 g/mol[1] and a persistence length of about 5 nm,[7] it is a extended random coil when viewed globally. Locally, however, it can be viewed as rodlike with a hydrodynamic radius, a, of approximately 0.5 nm and a monomer spacing of 0.252 nm.[1] However, only about 82% of the styrene aromatic rings are sulfonated[8] so the effective charge spacing can be taken to be 0.31 nm. Another complication is that the absolute intrinsic viscosities of long, flexible polymers are strongly shear dependent, and the BE modeling protocol is currently restricted to the zero shear limit.[5] At 0.003 M univalent salt, however, the double-layer thickness is comparable to the persistence length of PSS. For a thin charged rod under these conditions, the dependence of the electrical stress on shear rate is known to be weak,[9] and on that basis we may expect a relatively weak shear dependence of PSS under the experimental conditions employed.[1] Finally, although possible in principle, it is not possible in practice to carry out BE modeling of very long model structures due to the large number of plates required. We shall follow the approach of examining several simple model structures which vary in hydrdynamic radius, length, and curvature. Although absolute ξ's depend strongly on the specific details of model geometries, it shall be demonstrated that shape factor or intrinsic viscosity ratios as defined by eq 2 are fairly robust from one model to another. In addition, shear rate effects should also cancel out by taking viscosity ratios.

The four models studied are shown in Figure 1. The top two figures contain $n = 20$ elementary charges and consist of 144 plates. The uppermost figure has $a = 0.5$ nm, and the second has $a = 1.0$ nm. The lower two figures both have $a = 0.5$ nm and $n = 30$ and consist of 176 plates. The last structure (model IV) is curved to account for the effect of bending. For each model structure, the shape factor in the absence of ion relaxation, ξ_0, is determined, and these are given in Table 1. Ion relaxation is accounted for using small ion mobilities of Li^+, Na^+, K^+, and Cl^- derived from limiting molar conductivities.[5] The shape factors in different salt for the four different models are also presented in Table 1. Several conclusions can be drawn from this. First of all, the ξ's (and the corresponding [η]'s) are strongly dependent on model geometry. Second, given the substantial difference between ξ_0 and ξ in the various salts, the primary electroviscous effect is seen to be very large. For charged spherical particles, theory predicts that the primary electroviscous effect is significant when the equilibrium surface potential averaged over the particle surface, $\langle \Lambda_0 \rangle_S$, becomes large,[3,4] and we can expect this to be true for macroions in general. The average reduced equilibrium surface potential, $y_S = q\langle \Lambda_0 \rangle_S / k_B T$ (where q is the protonic charge, k_B is Boltzmann's constant, and T is absolute temperature), is substantial and equals −6.51, −4.26, −6.68, and −6.72 for models I through IV, respectively. For highly charged polyelectrolytes at low salt such as PSS studied in the present work, it is essential to account for electroviscous effects in modeling.

Table 2. Comparison of BE and Experimental Viscosity Ratios

model/experiment	X (LiCl, NaCl)	X (KCl, NaCl)
model I	1.11	0.88
model II	1.07	0.92
model III	1.10	0.90
model IV	1.10	0.90
experiment	1.08	0.87

If the shape factor or intrinsic viscosity ratios are considered following eq 2, the model dependence largely disappears, and this is shown by the first four entries in Table 2. This model independence of the viscosity ratios is important since it allows us to compare simple model results with actual experimental ratios. The last entry in Table 2 shows the ratio of experimental intrinsic viscosities. Clearly, there is good *quantitative* agreement between the model and experimental ratios. This analysis strongly supports the interpretation that the primary electroviscous effect is responsible for the differences in intrinsic viscosities of PSS in different monovalent salts. Furthermore, it demonstrates the usefulness of the continuum approach[10] in realistic modeling of the electroviscous effect. Specific ion effects also appear in related transport measurements such as free solution electrophoretic mobility. Ross and Scruggs[11] observed that the mobility of DNA in monovalent salt solutions at the same ionic strength increased in the order Li^+ to Na^+ to K^+. This is just the trend expected on the basis of the increase in limiting molar conductivities, reduction in distortion of the ion atmosphere, for the counterions in that order. It is interesting to point out, however, that Ross and Scruggs interpreted these results in terms of differences in counterion binding to DNA and not as a dynamic effect.

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