Revisit to the Intrinsic Viscosity–Molecular Weight Relationship of Ionic Polymers. 4. Viscosity Behavior of Ethylene Glycol/Water Solutions of Sodium Poly(styrenesulfonate)

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ABSTRACT: The viscosity of aqueous and ethylene glycol (EG)/water solutions of sodium poly(styrenesulfonate) was measured in the presence and absence of a foreign salt in the shear rate range of 100–1350 s^{-1}. The viscosity exhibited a substantial shear-thinning effect in both the water and binary solution at low-salt conditions: the effect was nearly independent of the EG content although the viscosity decreased markedly. With increasing salt concentration, the viscosity and the shear-thinning effect became smaller. Attention was drawn to the fact that the flexible ionic polymers and rigid ionic polymer latices displayed similar concentration and shear rate dependencies, which indicates that the conformation change effect invoked to explain the viscosity behavior of flexible ionic polymers does not play an important role.

Introduction

In our previous work on viscosity of ionic polymer solutions,[1-3] two important points were revealed; (1) qualitatively the same polymer and salt concentration dependencies of solution viscosity were observed for flexible ionic polymers and "rigid" ionic polymer latices, in contrast to Einstein's theory of viscosity,[4] and (2) the exponent α of the basic relation, $[\eta] = KM^{\alpha}$ ($[\eta]$ is the intrinsic viscosity, M is the molecular weight, and K and α are constants), was found for sodium poly(styrenesulfonate) (NaPSS) in salt-free solutions to be 1.2–1.6, instead of 2. It has been accepted that the change of the solution viscosity of flexible ionic polymers was accounted for in terms of dilation or shrinking of the molecular chain with concentrations.[5] The first finding above indicates that this interpretation needs to be reconsidered, since the same dependence was observed for nonflexible, rigid latices. Furthermore, we have come to understand that the ionic macromolecules are stretched out in salt-free solutions like rods. This understanding is also required to be reconsidered in light of the second finding. Since our findings are so contradictory to the widely accepted view, we need to confirm further the above-mentioned experimental results. Thus, in the present paper we studied the viscosity behavior of ethylene glycol (EG)/water solutions of NaPSS.

Experimental Section

A. Materials. Sodium poly(styrenesulfonate) (NaPSS; lot no. 17) was purchased from Pressure Chemical Co., Pittsburgh, PA. The sample was the same as that used in Part 2. An aqueous solution of the sample was dialyzed in a cellulose tube against purified water. The completeness of dialysis was judged by conductance measurements. The dialyzed sample was passed through a cation- and anion-exchange resin column several times. The amounts of loaded resins (IR-120B and IRA-400, Organo, Tokyo) were 5 times and $^1/_4$ times equivalent as much as the polyions, respectively. The ion-exchange resins used were washed by hydrochloric acid and aqueous solutions of sodium hydroxide repeatedly. The acid form of the polyelectrolyte thus obtained was immediately neutralized by an aqueous solution of sodium hydroxide (Merck, Darmstadt). Then the resulting NaPSS was freeze-dried and kept in a dark place with silica gel beads as a desiccating agent.

Characteristics of NaPSS used were already described in Part 2. The degree of sulfonation determined by conductometric titrations and SO_3^- analysis was 0.81. The weight-average molecular weight, M_w, was calculated to be 1.1×10^6 by using the degree of polymerization supplied by Pressure Chemical Co. and the degree of sulfonation thus obtained. From the brochure of the Pressure Chemical Co., M_w/M_n was below 1.10. The extinction coefficient ϵ_{262} at the peak top near 262 nm of NaPSS in aqueous solution was estimated to be 19.2 dL g^{-1} cm^{-1}, and the concentration of NaPSS in the viscosity measurements was determined spectrophotometrically by using this value. The water content of the dried sample was determined by the Karl–Fischer method to correct the sample mass in the estimation of the degree of sulfonation and ϵ_{262}.

Pyrex glass bottles washed by an ultrasonic device and rinsed with purified water were used for solution preparations. To minimize contamination by carbon dioxide, the bottles were filled with nitrogen gas during the solution preparation. Nitrogen gas was further blown into the bottles after the preparation.

The water used for solution preparation was purified by ion exchange, distillation, and subsequent ion exchange just prior to use, as described in Part 3. The water thus obtained had specific conductivities of $(0.5–0.6) \times 10^{-6}$ S cm^{-1}, which were practically the same as that of the water used in the previous work.

Ethylene glycol was purified by the same procedure as that described in Part 3. Some characteristics of the EG/water mixture at 25 °C were described in Part 3.

A suprapur grade sodium chloride (Merck, Darmstadt) was dried at 130 °C for at least 24 h, and a stock aqueous solution (0.1 M) was prepared.

B. Methods. Viscosity measurements were performed by using a precision rotational viscometer Haake RV20 system in the shear rate (q) range of 100–1350 s^{-1}. Temperature was controlled to be 25 ± 0.02 °C during the measurements. The details of the measurement and the determination of viscosity were described in Part 1. The viscometer was cleaned by using an ultrasonic device and washed with the purified water just prior to use, until the conductivity of the water becomes constant after washing.

Results and Discussion

Parts a and b of Figure 1 show the concentration dependence of the reduced viscosity (η_{sp}/C) for aqueous and 60 vol % EG solutions of NaPSS, respectively. In both the water and binary solutions, the reduced viscosity

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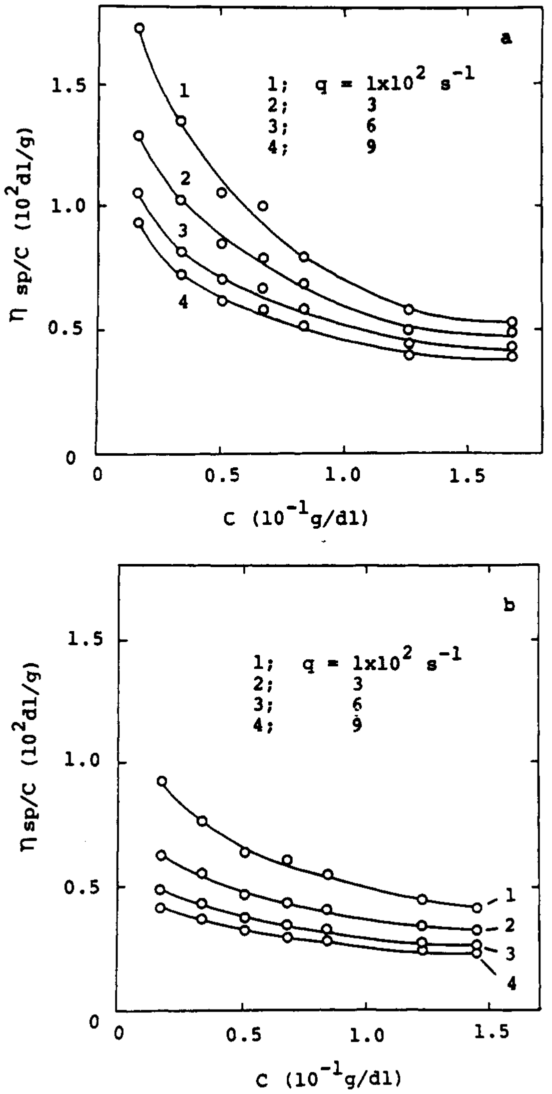

Figure 1. Reduced viscosity–concentration plot at various shear rates: (a) aqueous solution; (b) 60 vol % EG solution.

decreased with increasing polymer concentration (C) in the concentration range studied, and shear-thinning behavior, namely, a decrease of viscosity with increasing shear rate, q, was observed.[6] However, the reduced viscosity of the binary solution was smaller than that of the aqueous solution. The η_{sp}/C–q plots of various EG concentrations ($C = 8.4 \times 10^{-2}$ g/dL) are shown in Figure 2. The decrease of the reduced viscosity with increasing EG concentration was clearly demonstrated, and also the shear-thinning effect was substantial. In light of the experimental facts, we cannot accept the recent statement by Cohen and Priel that the shear-thinning effect is not important.[7]

It has already been reported that the viscosity of polyelectrolyte solution decreases with an increase in the content of an organic solvent. Fuoss et al. observed a decrease in the viscosity of a methanol/water solution of poly(vinylbutylpyridinium) bromide with an increase in the methanol concentration.[8] A similar behavior was also reported by Basu and Gupta for a dioxane/water solution of sodium carboxymethylcellulose.[9] The viscosity decrease was accounted for in terms of the decrease of the dielectric constant of the solvent, ϵ, with an increase in the methanol concentration: As ϵ decreased, more counterions were associated with the polyions, and the intramolecular electrostatic repulsive interaction between the ionized groups was diminished, allowing the chain to coil more compactly.[8] This assertion was in line with the interpretation for the concentration dependence of the reduced viscosity for salt-free aqueous solution of ionic polymers.[8]

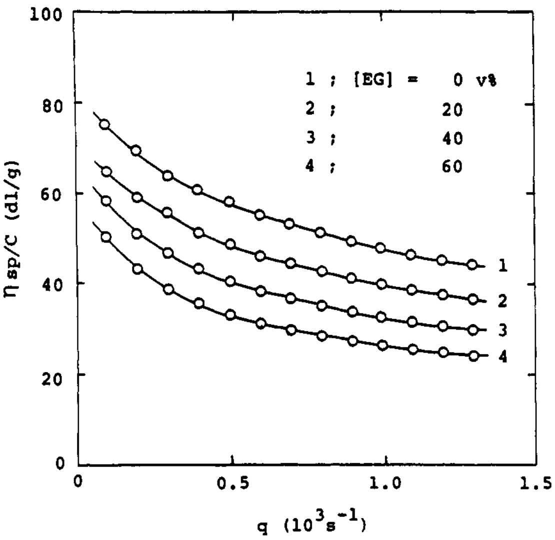

Figure 2. Influence of EG concentration on η_{sp}/C–q plot. $C = 8.4 \times 10^{-2}$ g/dL.

However, the accepted view may be shown to be invalid by examining the shear rate dependence of η_{sp}/C, to which due attention has not been paid. It is well-known that the influence of a shearing force on the solution viscosity becomes less substantial with decreasing anisotropy of molecules. Therefore, the solution is expected to become less shear-thinning with increasing [EG], if the decrease of the viscosity is caused by shrinking of the polyions. However, as can be seen from Figure 2, the influence of shear rate did not become smaller with an increase in [EG]. Further, as was reported in Part 3, the viscosity of ionic polymer latex suspensions also decreased with an increase in the EG concentration, although the conformational change may be negligible. In light of these experimental findings, we believe that the earlier interpretation in terms of the third-order electroviscous effect needs to be reconsidered.

Parts a and b of Figure 3 show the influence of the NaCl concentrations on η_{sp}/C–q plots for aqueous and 40 vol % EG/water solutions of NaPSS. With an increase in the NaCl concentration, the reduced viscosity decreased and the solution approached Newtonian fluid in both the aqueous and binary solutions.

The existing interpretation[9] for the salt concentration dependence of the viscosity of ionic polymer solution is also based on the conformational factor, as was the case for the EG concentration dependence. With an increase in the concentration of added salt, the intramacroion repulsive electrostatic interaction becomes shielded, causing shrinking of the polyions, and accordingly the viscosity decreases. At first sight, the above-mentioned decrease of the shear-thinning behavior with an increase in the salt concentration seems to support this claim. However, essentially the same salt concentration dependence was observed also with latex suspension. Thus, the previous interpretation again encounters a difficulty.

The similarity between the viscosity behavior of linear polyelectrolyte solution and that of ionic latex suspension suggests that the first- and second-order electroviscous effects, namely, the viscosity increments due to the polyion–counterion and polyion–polyion electrostatic interactions, play important roles in linear polyelectrolyte solution. Of course, the third-order electroviscous effect cannot completely be ruled out, though it is not as

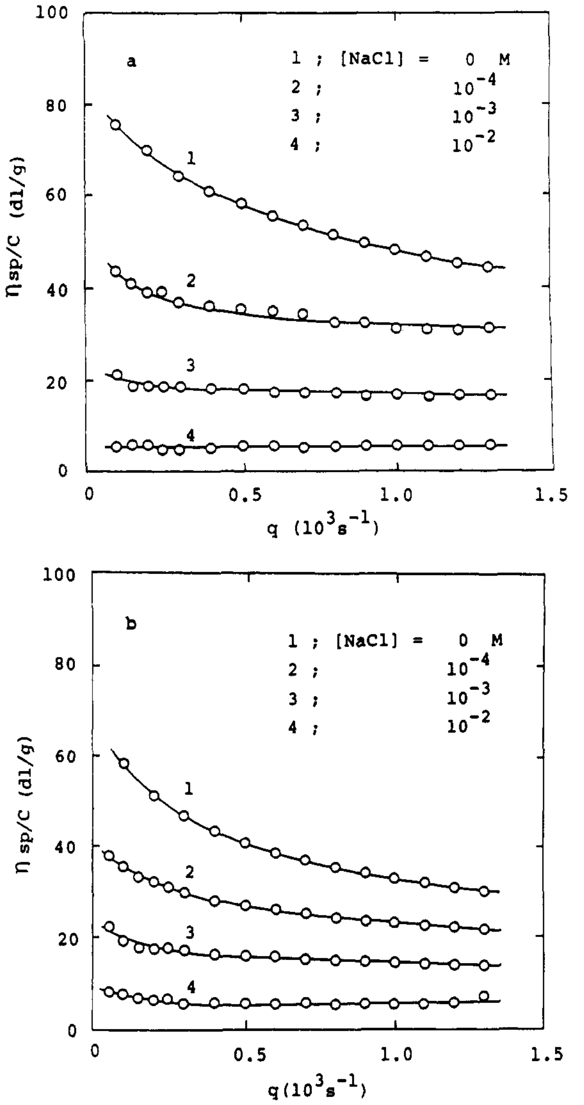

Figure 3. η_{sp}/C plotted against q at various NaCl concentrations: (a) aqueous solution; (b) 40 vol % EG solution. $C = 8.4 \times 10^{-2}$ g/dL.

influential as widely believed. In addition, there is another important factor, namely hydrodynamic effects. (The importance of the hydrodynamic effects can be clearly shown by the molecular weight dependence of the viscosity, for instance.)

In order to elucidate the electroviscous effects, the viscosities of the aqueous and binary solutions were plotted as a function of log [NaCl] in Figure 4. At [NaCl] = 10^{-2} M, where the solutions exhibited no shear rate dependence, namely, a Newtonian behavior, the viscosities are independent of the solvent system. This observation shows that the electroviscous effects, which should be sensitive toward solvent properties, such as ϵ, are absent at 10^{-2} M NaCl. Then the viscosity of the 10^{-2} M solution must be accounted for in terms of solely hydrodynamic effects.

In connection with this, we point out that, even at [NaCl] = 10^{-3} M, the viscosity of dilute aqueous suspensions of an N-100 latex (diameter, 0.12×10^{-6} m; charge density, 5.64×10^{-6} C/cm^2) was very close to the Einstein theoretical value, which was calculated on the basis of the hydrodynamic effect for an isolated sphere.

Concluding Remarks

In the present paper, the viscosity behavior of ethylene glycol/water solutions of sodium poly(styrenesulfonate) was investigated in the presence and absence of a simple salt. The [EG] dependence and the [NaCl] dependence of the viscosity of NaPSS solution were essentially the same as that for the ionic latex suspension reported in Part 3, including the shear rate effect. This finding is obviously in contradiction to the existing interpretation of the viscosity behavior of polyelectrolyte solution, in which both the solvent effect and salt concentration dependence were explained in terms of the third-order electroviscous effect caused by repulsive intramacroion interaction between the ionized groups. From the comparison of the salt concentration dependence of the viscosity of aqueous and binary solutions, it was shown that the hydrodynamic effects played principal roles at sufficiently high salt concentration.

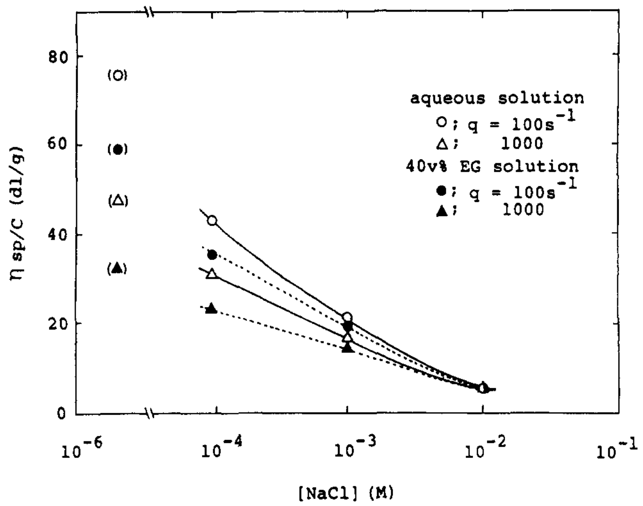

Figure 4. Reduced viscosity plotted against log [NaCl] at various shear rates. The data in the brackets are those in water ([H$^+$] = 1.4×10^{-6} M). $C = 8.4 \times 10^{-2}$ g/dL.

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(6) The viscosity obtained in the present experiment was smaller and less shear-thinning than that in our previous data. It might be due to the trace of ionic impurity that could not be eliminated during the present purification process. The discussion will be thus restricted to qualitative ones, taking into account the possible contamination by the ionic substance in the sample.
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Registry No. NaPSS, 9080-79-9; H_2O, 7732-18-5; $HO(CH_2)_2OH$, 107-21-1; NaCl, 7647-14-5.