

Review

On the solution viscosity of ionic polymers and their conformation in solutions

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Abstract: The viscosity behavior of linear, flexible ionic polymers in solutions and its accepted interpretation were discussed. Experimental viscosity data by Yamanaka *et al.* were pointed out to show the α value of the Houwink-Mark-Sakurada equation being smaller than two, a value expected for rod-like conformation. The viscosity of latex dispersions, telechelic polymer solutions, and microgel dispersions showed that the intra-molecular interaction does not play a role as important as was supposed to be in the previous argument. The Booth theory of primary electroviscous effect of charged particles (distortion of ion cloud under flow) was found to be satisfactory in explaining dependencies of viscosity of colloidal particles on charge number (Q), size, and salt concentration, particularly for large κa ($1/\kappa$: Debye's radius, a : the particle radius) and at small Q . Taking into consideration that the macroion domain corresponds to extremely high concentrations of ionic groups, the formation of multiple ions by a counterion-mediated attraction, which was not considered so far, was tentatively suggested. Further, the contribution of localized ordered domains of macroions that were recently unveiled was suggested to be presumably influential in viscosity properties.

Key words: Reduced viscosity; ionic polymers; Houwink-Mark-Sakurada equation; rod-like model; electroviscous effect; localized ordered structure; colloidal particles.

Introduction. One of the central problems in macromolecular science has been to assess the size and shape of macromolecules in solutions. A convenient method for this purpose is the viscosity measurements: the limiting viscosity number $[\eta]$ is related to the molecular weight M by the Houwink-Mark-Sakurada (HMS) equation, $[\eta] = KM^\alpha$, where K and α are constants.¹⁾ The theoretical analysis shows that α takes values of 2, 0.8–0.5, and 0 for rod, random coil, and sphere, respectively.²⁾

In their pioneering work^{3),4)} by Fuoss, Doty, and Katchalsky, the HMS equation was applied for ionic polymer solutions. Oth and Doty found that, when polymethacrylic acid was neutralized with sodium hydroxide, the α value increased steadily from 0.82 for the unneutralized acid to 1.87 for the almost neutralized case. According to Fuoss,³⁾ this result was taken as implying that highly charged macroions *at infinite dilution* had the shape of an extended rod. This interpretation was rationalized as follows: "as the (polymer) concentration decreases, more and more counterions leave the polyion, resulting in an increase in intramolecular repulsion in each coil as

increasingly more electric charges on the chain become uncompensated. Thus the coil will stretch and the reduced viscosity will increase". This interpretation was accepted widely and was succeeded to later generations. Noteworthy is the fact that Fuoss' remark on the concentration was ignored in recent work and linear flexible macroions are described as stretched rods even at finite concentrations. Whether this is correct or not, there is a point to be considered critically, which we would like to ponder in this article.

The maximum in the reduced viscosity-concentration curve and the conformation of macroions. The above-mentioned argument was based on the limiting viscosity number obtained by the so-called Fuoss plot, which implies that the reduced viscosity η_{sp}/C increases monotonously with decreasing polymer concentration (C). Truly, this concentration dependence was found to be valid over a wide range of variable.³⁾ However, soon thereafter several investigators started to report that the monotonous increase was not real; instead, the η_{sp}/C - C curve displayed a maximum at very low polymer

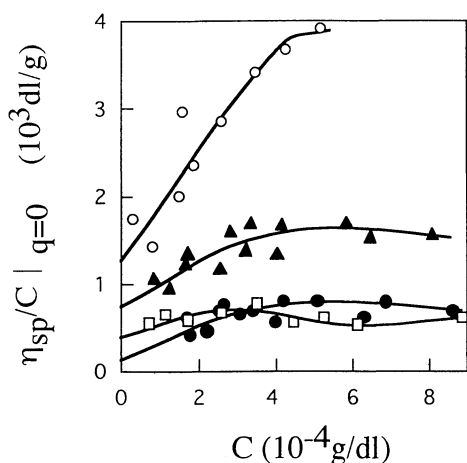


Fig. 1. The reduced viscosity of sodium poly(styrene sulfonate)s at zero shear rate (q) versus concentration at 25°C: Open circles; $M_w = 1.7 \times 10^6$, degree of sulfonation (DS) = 0.88, filled triangles; $M_w = 1.1 \times 10^6$, DS = 0.81, open squares; $M_w = 6.7 \times 10^5$, DS = 0.73, filled circles; $M_w = 3.7 \times 10^5$, DS = 0.85. The reduced viscosity was measured at various shear rates and extrapolated to zero rate. Taken from Ref. 10 with the permission of the American Chemical Society.

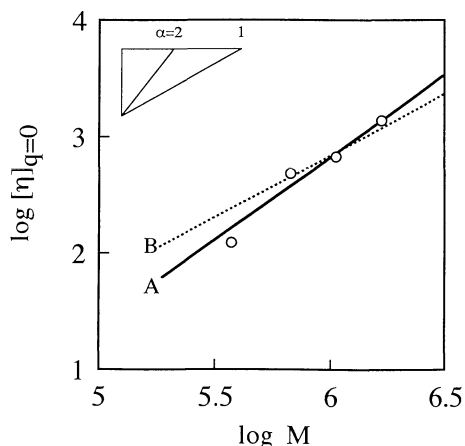


Fig. 2. The limiting viscosity number versus molecular weight plot for poly(styrene sulfonate)s. solvent: water, temperature: 25°C. open circles: observed. See the text for the lines A and B. Taken from Ref. 10 with the permission of the American Chemical Society.

concentrations.^{5)–8)} If the maximum truly exists, the above-mentioned argument on the macromolecular shape has to be reconsidered. Recent viscosity measurements clearly substantiate the presence of the maximum,^{9),10)} Fig. 1 shows the reduced viscosity in the concentration region below the maximum for poly(styrene sulfonate)s of various molecular weights.¹⁰⁾ Clearly, the viscosity decreases with decreasing concentration, indicating that the concentration dependence is *not* reproducible by the Fuoss plot and $[\eta]$ determined thereby has to be viewed

with caution. Thus, Yamanaka *et al.* evaluated $[\eta]$ by the third-order least-squares method of the data of Fig. 1.

The $[\eta]$ thus determined is plotted against the molecular weight in Fig. 2. The line A, which was obtained by the first-order least-squares method, has a slope of 1.6. When the lowest molecular weight data is put out of consideration because of its larger error in the viscosity measurements, the slope value is 1.2 (the line B) from the three molecular weight samples. In both cases, the slope is far smaller than two. In this respect, we note that Vink obtained 1.1 for the slope for sodium carboxymethylcellulose of a relatively small degree of substitution.⁹⁾

The fact, that the slope values smaller than two are found, indicates the earlier reasoning on the macroion conformation needs reconsideration, as far as the HMS equation can be applied also for ionic macromolecules. One of the simplest interpretations is that the macroions are not fully stretched out even at the infinite dilution, at variance with the argument in early 50's. Based on the sedimentation coefficients, Butler *et al.* also advanced a view that poly(styrene sulfonate) ions have a maximum end-to-end distance less than half the contour length.⁸⁾

The concentration dependence of the reduced viscosity. As mentioned above, the reduced viscosity steeply increases with decreasing concentration in the concentration range above the maximum. This increase was taken as due to elongation of the macroion chain, which was caused by progressively enhanced dissociation of ionizable groups and hence intensification of the intramolecular repulsion.³⁾ In short, the viscosity increase was attributed solely to the intramolecular interaction. However, this interpretation seems to be reconsidered since a similar concentration dependence can be observed for dispersions of practically undeformable colloidal particles and for solutions of polymers containing only a single ionizable group per chain as follows.

(1) *Viscosity of latex dispersions.* Yamanaka *et al.* found that the reduced viscosity of aqueous dispersions of ionic latex particles (diameter: 0.1 μm) was much higher than the Einstein prediction^{2a)} and displayed a very similar concentration dependence as flexible ionic polymers.¹¹⁾ Because it is most implausible for crosslinked latex particles to shrink or swell with changing concentration to the same degree as linear macroions, it would not be reasonable to regard their conformational change as the main factor of the observed concentration dependence for linear macroions. In other words, the intra-molecular interaction is not so important as was previously considered.

(2) *Viscosity of telechelic polymers.* Hara *et al.*

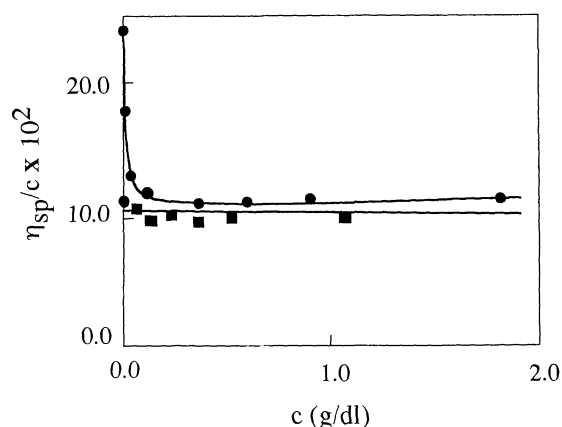


Fig. 3. The reduced viscosity for monofunctional telechelic polymer in dimethyl formamide (top) as well as for uncharged polymer (bottom). Taken from Ref. 12b) with the permission of the American Chemical Society.

synthesized ω -dimethylamino-polystyrene, a telechelic polymer, by anionic polymerization technique, which contained only a single amino group at one end in each polymer molecule¹²⁾ and measured the viscosity of its dimethyl formamide solutions. The results are shown in Fig. 3. When the polymer was in an uncharged state, in other words, when the amino group was not quaternized, the η_{sp}/C was linear with C . On the other hand, when the polymer was quaternized and ionic, the η_{sp}/C sharply decreased with C as mentioned above for ionic polymers. Since only one ionic group is present in one polymer molecule, an *intramolecular* electrostatic interaction is definitely inconceivable; the η_{sp}/C decrease observed has to be ascribed to an *intermolecular* interaction in disagreement with the accepted view.

(3) *Viscosity of microgel dispersions.* Spherical poly(styrene sulfonate) particles in the radius range between 0.0070 and 0.0500 μm were synthesized via crosslinking in microemulsion and subsequent sulfonation.¹³⁾ The aqueous solutions of these microgels also showed high viscosities with a marked decrease of η_{sp}/C with increasing C . Since conformational changes play only a minor role for these systems, it was concluded that the major contribution to the observed viscosity behavior was an intermolecular interaction, as was found for latex and telechelic polymer systems.

The dependence of the reduced viscosity on charge density, size and salt concentration. In the above section, it was demonstrated that the reduced viscosity does not reflect directly the conformational change due to intra-molecular interaction. The next question is how the *inter-macroion* interaction then

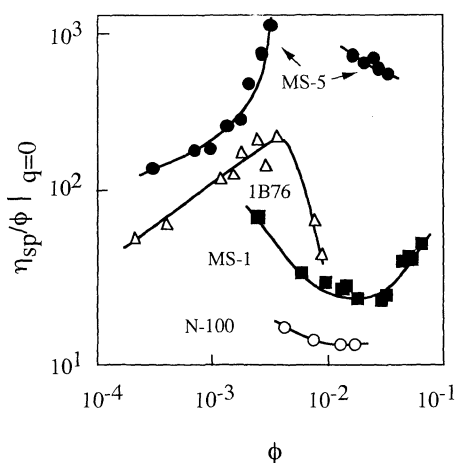


Fig. 4. The reduced viscosity extrapolated to zero shear rate for no-salt dispersions of various latices having a constant diameter at 25°C. Samples: MS-5 (charge density $\rho = 0.82 \mu\text{C}/\text{cm}^2$, diameter $d = 0.1 \mu\text{m}$), 1B76 ($\rho = 0.88$, $d = 0.11$), MS-1 ($\rho = 3.65$, $d = 0.13$), N-100 ($\rho = 5.64$, $d = 0.12$). Taken from Ref. 11 with the permission of Academic Press.

determines the viscosity behavior. To answer this question seems to be formidable at present but it is worth mentioning exploratory experimental facts that the present author believes is of great implication to the complete understanding of viscosity behavior of macroionic solutions. First it is seen from Yamanaka *et al.*'s viscosity data for latex particle dispersions (Fig. 4) that, at a given volume fraction of the particles and at a constant size, the reduced viscosity becomes *smaller* with increasing charge density.

The size dependence was studied by Antonietti *et al.*¹³⁾ for microgel systems, as shown in Fig. 5. The reduced viscosity becomes *smaller* with increasing size. This is rather surprising at the first sight since it differs from our tacit understanding on the basis of the HMS equation, which indicates that, roughly speaking, the viscosity becomes larger with increasing molecular weight, and hence hydrodynamic volume. Thus other factors that are not involved in non-ionic polymers, namely in the HMS equation, appear to play important roles for ionic systems.

The salt concentration dependence of the reduced viscosity of latex dispersions is shown in Fig. 6. The viscosity decreases with increasing salt concentration and approaches the Einstein behavior. A qualitatively same trend was noticed also for linear macroions and was attributed to shrinking of the macroion chain in saline solutions. Since the size of colloidal particles hardly or only slightly changes with salt addition, the shrinking factor would not be the main cause of the viscosity decrease.

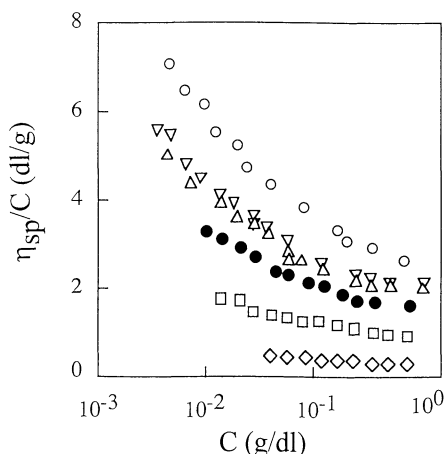


Fig. 5. The reduced viscosity of microgels of various sizes. (○) radius $a=0.0119 \mu\text{m}$, (∇) $a=0.0251$, (Δ) $a=0.0273$, (●) $a=0.0374$, (\square) $a=0.0525$, (\diamond) $a=0.0678$. Taken from Ref. 13 with the permissions of the original authors and the American Institute of Physics.

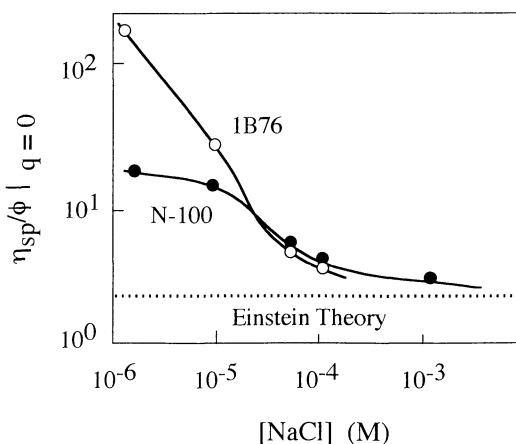


Fig. 6. The reduced viscosity extrapolated to zero shear rate (q) of latex dispersions plotted against NaCl concentration at 25°C and at a volume fraction of 0.0040. Latex: 1B76 ($d=0.11 \mu\text{m}$, $\rho=0.88 \mu\text{C}/\text{cm}^2$), N-100 ($d=0.12 \mu\text{m}$, $\rho=5.64 \mu\text{C}/\text{cm}^2$). The data in the brackets are those in water. Taken from Ref. 11 with the permission of Academic Press, New York.

Role of the distortion of the ion cloud under flow in viscosity behavior: primary electroviscous effect. The viscosity of uncharged spheres was treated by Einstein, who theoretically demonstrated that the reduced viscosity is 2.5, independently of the sphere concentration.^{2a)} As shown above the reduced viscosity of charged particles was always larger than 2.5. In order to explain this difference, it was proposed that the charged spheres be treated as those of radii of hard sphere radius (a) plus $1/\kappa$ ($1/\kappa$: the Debye radius).¹⁴⁾ Although the seemingly satisfactory agreement with observation has

been claimed for various cases, this model is obviously inconsistent with the presence of the maximum in the viscosity curve, since $(a+1/\kappa)$ simply decreases with increasing concentration without showing a maximum. Furthermore, as pointed out by us earlier,¹⁵⁾ this mental exercise contradicts with the proverbial analysis by Perrin¹⁶⁾; he would have had failed to obtain correctly Avogadro's number from sedimentation equilibrium of colloidal particles, if he had adopted the enlarged sphere concept.

The concept of the ionic atmosphere (or cloud) was introduced by Debye and Hückel,¹⁷⁾ and its radius ($1/\kappa$) is determined by a balance of thermal energy of ions and electrostatic interionic interaction. The ionic atmosphere does not represent a rigid shell; it cannot and should not be regarded as a body exerting hydrodynamic resistance in flow. It keeps usually the spherical symmetry around a central ion but it is distorted when solvent is in flow. When distorted, the total system would experience an extra energy dissipation. This effect, as often referred to as primary electroviscous effect, causes viscosity increments. Booth formulated a theory¹⁸⁾ of this phenomenon for dispersions of charged spheres, according to which $[\eta]$ of charged particles is given as follows:

$$[\eta] = 2.5 [1 + C_1 (Qe^2 / \epsilon akT)^2 Z (\kappa a)] \quad [1]$$

with

$$C_1 = (\epsilon \kappa T / \eta_0 e^2) [\sum n_i z_i^2 w_i^{-1} / \sum n_i z_i^2] \quad [2]$$

$$\kappa^2 = (4 \pi e^2 / \epsilon \kappa T) \sum n_i z_i^2 \quad [3]$$

where Q is the effective charge number per particle, η_0 the solvent viscosity, e the elementary charge, ϵ the dielectric constant of the dispersion medium, κ the Boltzmann constant, T the temperature, N the number of ionic species, and n_i , z_i , and w_i are the number concentration, valency, and mobility of the ions of species i , respectively. The first term of the right-hand side of Eq. [1] corresponds to the hydrodynamic effect considered by Einstein and the second term is the electroviscous effect. The deformability of the counterion cloud is given by the function $Z(\kappa a)$, which increases monotonically with decreasing κa , as shown in Fig. 7.¹⁹⁾ It is seen that the Booth prediction agrees with observed values at large κa . This is reasonable in light of the assumptions made in the derivation of the theory, though the original paper should be referred to for details. The κa dependence of $Z(\kappa a)$ is consistent with the above-mentioned dependence on charge number and salt concentration of the viscometric

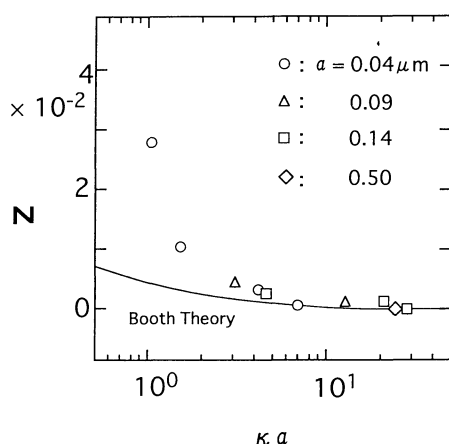


Fig. 7. Observed and theoretical electroviscous effects $Z(\kappa a)$ plotted against κa for dispersions of four kinds of colloid particles having various radii at various salt concentrations and at a volume fraction of 3.5×10^{-3} . Taken from Ref. 19 with the permission of the American Physical Society.

Table I. Influence of the effective charge number on the electroviscous effect

Latex	Q	Salt Conc. (M)	$[\eta]_{\text{expt}}$	$[\eta]_{\text{Booth}}$
1P30 ($a: 0.055 \mu\text{m}$)	300	5×10^{-5} 10^{-4}	3.1 3.0	2.6 2.6
1B76 ($a: 0.055 \mu\text{m}$)	800	5×10^{-5} 10^{-4}	2.9 2.9	3.4 3.0
N-100 ($a: 0.060 \mu\text{m}$)	2800	5×10^{-5} 10^{-4}	3.6 3.1	11.0 7.2

behaviors so that we are inclined to judge that the distortion of the ion cloud is one of the influential factors to be first addressed to get the correct understanding of the viscosity properties of charged systems.

Furthermore, the theory is found to be satisfactory for small Q , as shown in Table I. For N-100, which is much more highly charged than other latices 1P30 and 1B76, particularly at lower salt concentration, the discrepancy between theory and experiment is large.

It is clear now that the Booth theory is quantitatively justified at large κa and small Q . Yamanaka *et al.*'s work^{20,21)} also showed that the theory can satisfactorily account for the influence of other parameters such as η_0 , ϵ , and w_i on the electroviscous effect. Accepting the success of the Booth theory for charged particles, it is tempting to ascribe the observed concentration change of the reduced viscosity of *linear, flexible ionic polymers* to the distortion of the ion cloud. We will come back to this problem later.

Further discussion on the rod-like conformation of flexible macroions. As discussed above, the treatment of solution viscosity data of flexible polyelectrolytes needs to be in part modified and too much emphasis should not be placed on the role of the intra-molecular interaction. There are still other related features to be considered carefully, which we wish to dissect here.

As mentioned above, it was widely believed that the flexible macroions assume fully stretched conformation as a result of repulsive interaction between ionized groups inside the macroion. Certainly, such an intra-molecular repulsive interaction is real as far as the ionized groups carry like charges. However, all ionic systems are governed by the principle of electric neutrality. In other words, the total systems must contain the "like charges" and an equivalent amount of "unlike charges", wherever they are. In such systems, according to Feynman,²²⁾ "attraction arises, because the repulsion of likes and attraction of unlikes will tend to bring unlikes closer together and push likes farther apart." Such an attraction is frequently noticed as follows: The first example is the formation of multiple ions at concentrations higher than the Debye-Hückel regime.²³⁾ Below 10^{-3} M for 1-1 electrolytes in water, complete dissociation takes place so that the Debye-Hückel theory is valid. Above this concentration, however, some portions of free ions tend to form triple ions, which are possible due to an attraction between two like-charges through the intermediary of one unlike charge present in between; a counterion-mediated attraction is generated. Another manifestation is hydrogen bonding, in which two anions (for example O^-) attract each other through H^+ . The stability of ionic crystals is due to this type of attraction; Na^+ attracts Na^+ through Cl^- to maintain NaCl crystal. The atomic nucleus attracts another nucleus by electrons so that molecules are stable: As a matter of fact, the Hamiltonian of the Schrödinger equation for hydrogen molecules definitely shows that the repulsion between like charges is overwhelmed by the attraction between unlikes. The counterion-mediated attraction was also demonstrated by the author to be important in colloidal and macroionic solutions.²⁴⁾

It is important to recall here that macroion domains correspond to very high ionic concentrations. The following approximate estimate would be helpful. For fully neutralized polyacrylate ions, the distance between neighboring COO^- groups is about 2.5 Å. On the other hand, for 10 M solution of 1-1 type electrolytes, the distance between two anions is about 5.5 Å. Thus, the concentrations of COO^- groups in the vicinity of the polymer chains correspond to $\gg 10$ M of 1-1 electrolytes.

For NaCl, the solubility in water is 27 g (0.46 moles) in 100 g solutions, so that the above-mentioned concentrations such as 10 M and $\gg 10$ M can never be realistic. It is nevertheless most difficult to rationalize that ionic concentrations in the vicinity of macroions can be lower than 10^{-3} M so that the complete dissociation of the ionizable groups may be assumed and only repulsive interaction is generated between the groups, as was claimed in the previous argument, considering that the Debye-Hückel theory is valid below 10^{-3} M for 1-1 electrolyte solutions.

Once the multiple ionic aggregates are formed, the macroions are expected not to be stretched out but rather coiled up. The α value (1.2 ~ 1.6) of the HMS equation found by Yamanaka *et al.* for sodium poly(styrene sulfonate)s seems to be consistent with this idea. In this respect, it is worth mentioning recent computer simulation work,²⁵⁾ which clearly indicated that linear ionic chains are coiled up in accordance with our reasoning.

If the coiling-up actually takes place, it would not be so unreasonable to invoke the distortion of the ion cloud to account for the viscometric behavior of linear, flexible macroions, though no theoretical treatment has been advanced for such systems.

Localized ordered structures in polyelectrolyte solutions. The above discussion was based on a premise that the solution viscosity depends on an isolated polymer chain and coexisting neighboring chains. This would be definitely acceptable for uncharged, neutral polymers. However, it is not finally certain that the same is true for ionic systems, because the interaction involved is of long-range and intensive. In this respect, it seems to be important to give thought on the putative influence of ordering phenomena of macroions in dilute and low salt solutions. Recent systematic studies by scattering techniques and video microscopy showed that electrically charged solute entities form ordered structures, though in solutions.²⁶⁾ Flexible macroions are not exceptions. The X-ray, neutron and light scattering profiles of their solutions show distinct peak(s) at low salt conditions. Furthermore, the spacing between the macroions ($2D_{\text{exp}}$), which can be obtained by the peak position and the Bragg equation, was found to be systematically smaller than the average spacing ($2D_0$) that can be estimated from the concentration assuming a uniform distribution throughout the solution. The $2D_{\text{exp}} < 2D_0$ relation implies that the ordered structures are not space-filling but localized.

The size of the localized structures is difficult to accurately determine, but the following neutron scattering data appears to provide approximate information. For

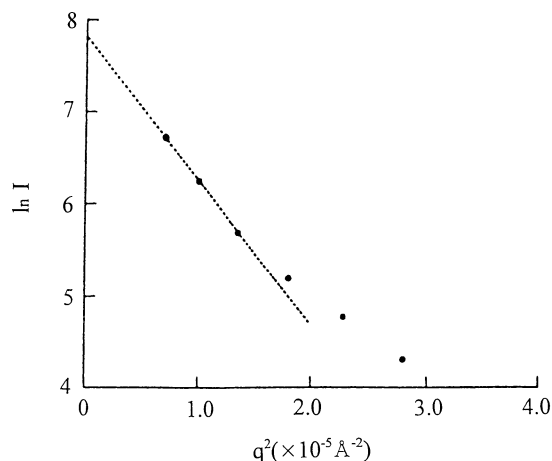


Fig. 8. Guinier plot of small-angle neutron scattering curve of a D_2O solution of sodium poly(styrene sulfonate). [polymer] = 0.04 g/ml. Taken from Ref. 27 with the permission of the American Chemical Society.

sodium poly(styrene sulfonate)- D_2O solutions, Matsuoka *et al.*²⁷⁾ found a sharp upturn at very low scattering vectors of the neutron scattering. Such an upturn is indicative of structural inhomogeneities such as the two-state structure. The size of the localized ordered structure can be estimated, though approximately, by the Guinier plot of the upturn. Fig. 8 shows such a plot, from which the radius of gyration R_g of the localized ordered structure is obtained by

$$I(q) = I(0) \exp [-(1/3) R_g^2 q^2] \quad [4]$$

where q is the scattering vector. The R_g was found to be $0.0686 \mu\text{m}$. Assuming that the ordered structure is spherical, the radius R of the structure can be estimated to be $0.0886 \mu\text{m}$ by using $R^2 = (5/3) R_g^2$. Because $2D_{\text{exp}}$ was $0.0085 \mu\text{m}$ from the peak position, though the scattering profile is not given here, the average number of macroions in one ordered structure (N) is 4,700 under the experimental conditions adopted. Table II summarizes the results for other conditions.

The above results were obtained at polymer concentrations of 0.01 ~ 0.08 g/ml. Because of the technical problems, it is difficult to carry out the neutron scattering experiments at much low concentrations where the viscosity measurements are done. Thus, the N values estimated above would not be true for the conditions of the viscosity measurements. However, the existence of the localized ordered structure in such low concentrations is highly plausible in light of the experimental finding by the following dynamic light scattering data. Sedlak and Amis²⁸⁾

Table II. Structural parameters of the localized ordered structures and the number of macroions inside for D₂O-poly(styrene sulfonate) solutions

[Polymer] (g/ml)	[NaCl] (M)	R _g (μ m)	R (μ m)	2D _{exp} (μ m)	N
0.01	0	0.0407	0.0525	0.0166	130
0.02	0	0.0516	0.0666	0.0103	1100
0.04	0	0.0686	0.0886	0.0085	4700
0.08	0	(0.0630)	(0.0813)	(0.0064)	(8600)
0.04	0.05	0.0664	0.0857	0.0094	3200
0.04	0.1	0.0683	0.0882	(0.0132)	(1250)

The data in parentheses contain larger uncertainties than other cases because of the broadness of the Bragg peak.

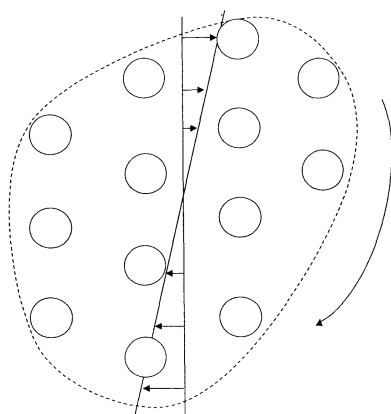


Fig. 9. A localized ordered structure in flow. The circles conveniently represent macroions forming an hexagonal arrangement.

found two diffusion constants (fast and slow) for poly(styrene sulfonate) solutions at low salt conditions in the polymer concentration range between 0.00001 and 0.01 g/ml, which largely overlaps with the concentration range for the viscosity measurements. According to our interpretation, the slow mode corresponds to the molecular motion in the ordered state and the fast one to the free macromolecules. Thus, we may expect the presence of localized ordered regions also in the concentration range for the viscosity measurements. If this is correct, the localized ordered structure in flow will be a source of additional energy dissipation, causing viscosity enhancement, as is highly schematically demonstrated in Fig. 9. It has to be pointed out that this suggestion is based on our basic understanding of the energy dissipation in neutral polymer chain solutions. However, it is not clear at present how the energy dissipation in the present case is related to the rotation of the localized ordered structure. Furthermore, the contribution of *flow-caused* rupture and/or

formation of the ordered domains cannot be ruled out, which would cause changes in the energy state of the total systems, and therefore would have some influence on the solution viscosity.

Concluding remark. In the preceding sections, we discussed the currently accepted interpretation of some viscometric properties of linear, flexible macroions. Recently obtained experimental facts indicate that the interpretation has to be re-considered at least in part and we proposed an alternative. However, the new interpretation is yet to be established. In order to stimulate discussion on the topic, it seems appropriate to sum up our stance in a rather critical manner as follows: The α value of the HMS equation was determined to be 1.2~1.6, being smaller than two, for sodium poly(styrene sulfonate)s and suggesting that the macroions are not fully stretched. This argument is based on the assumption that the HMS equation is valid for ionic systems as well as for non-ionic systems. Whether this assumption is correct or not cannot be judged because only the hydrodynamic interaction between polymer chains and solvent has been taken into consideration in the HMS equation. Certainly this type of interaction is present in ionic polymers, but on the basis of the success of the Booth theory on primary electroviscous effect (distortion of ion cloud) for charged particles at large κa and small Q , we cannot be sure whether the hydrodynamic effects considered in the HMS equation are adequate also for description of ionic polymers. In other words, it is difficult to account for the observed size dependence of viscosity in terms of the concept underlying the HMS equation. This is also the case for Einstein's viscosity equation (a special case of the HMS equation), which shows that viscosity is *independent* of the solute size. On the other hand, the Booth theory of the distortion of ion cloud was demonstrated to satisfactorily account for the size and salt concentration dependence for

large size, high salt concentration and low charge number. Although a complete theory, which is valid in a more wide range of parameters, and also the one for linear, flexible macroions, are awaited for, the influence of the distortion of ion cloud is not considered in the hydrodynamic analysis for non-ionic polymers, and therefore the application of the HMS equation for ionic systems seems to be not fully justified.

Thus, we are faced with a paradoxical situation. To reach the complete understanding of the problem, it seems that more general points of view must be brought into argument. From the experimental point of view, the formation of the putative ionic aggregates inside the macroion domain seems to be worth being scrutinized. If it can be detected, it would provide an answer to the pros and cons, first of all, of the rod-like conformation and of the existing interpretation of viscosity behavior of linear, flexible macroions.

We proposed also to newly consider the influence of the localized ordered structures upon the viscometric properties of macroion solutions. Various experimental techniques and model experiments using "visual" colloidal particles show that the ordering phenomenon is real. However, except Staudinger,²⁹⁾ no one has considered the relevance of this phenomenon to viscometric properties. It is highly instructive to refer here to Staudinger's statement made in 1931 as follows:

"Like in sodium chloride solutions, negatively charged chloride ions are gathered around positively charged sodium ions as a result of electrostatic attraction and/or repulsion and positively charged sodium ions around negatively charged chloride ions. Thus, a certain type of ionic distribution would be established as a stationary state. A similar effect would take place for dissociated polyacrylic acids. Since the polyacids are stretched, polyvalent chain molecules, the polyacids would be fixed to each other by ionic charges. This fixation becomes stronger with increasing molecular length. Such a stationary state in solutions corresponds to some sort of structure formation. The distortion of the structure by the flow in viscometer will encounter resistance and hence cause higher viscosity."

This topic is worth more detailed experimental and theoretical elucidation. In this respect, we recall that the established concept in colloid science, namely the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, was pointed out by the present author to be satisfactory for description of the ordering phenomena in rather concentrated dispersions, although it is not so for dilute dispersions, where it was found that a new factor has to be supplemented to the classical DLVO formalism. It is

likewise interesting to dissect what a kind of new factor(s) is to be introduced into the HMS equation, which has been established for neutral polymer systems, if it is intrinsically correct also for ionic polymers. Hopefully, the present article triggers further consideration on this matter.

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