

ANALYSIS OF VISCOSITY ABNORMALITIES OF POLYELECTROLYTES IN DILUTE SOLUTIONS*

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Abstract It was found that the interface effects in viscous capillary flow influenced the process of viscosity measurement greatly, and the abnormal viscosity behaviors of polyelectrolytes as well as neutral polymers in dilute solution region were ascribed to interface effect. According to this theory, we have reviewed the previous viscosity data of derivatives of poly-2-vinylpyridine reported by Maclay and Fuoss first. Then, the abnormal viscosity behaviors of a series of sodium polystyrene sulfonate samples with various molecular weights in dilute aqueous solutions were studied further. The solute adsorption behaviors and structural information of polymers have been discussed carefully.

Keywords: Polyelectrolytes; Abnormal viscosity behaviors; Polyelectrolyte effect; Interface effect.

INTRODUCTION

Polyelectrolyte is a type of polymer with positive or negative charges on its repeating units. It dissociates in water or lower alcohol, forming a charged poly-ion surrounded by an atmosphere of small, mobile counter ions. For bearing both features of polymer and electrolyte molecules, polyelectrolytes have very extensive and important applications in various fields^[1–4].

However, applications of polyelectrolyte materials are mostly carried out in solutions. It is undoubtedly significant to understand the properties of polyelectrolyte solutions well for further expanding their applications. But, until now, researchers know and understand less about polyelectrolytes than neutral polymers. Early in 1940s when Fuoss^[5] did research on viscosity of polyelectrolyte solutions, a phenomenon was found that the reduced viscosity increased as solution was diluted, which was totally different from that of neutral polymers. In literatures, it is defined as “polyelectrolyte effect”^[1]. Most researchers thought that, the more dilute solutions were, the larger intra-chain electrostatic repulsion existed, which resulted in chain extension and the increase of reduced viscosity upon dilution. This viewpoint was generally accepted by researchers over the world for more than 60 years, and has been cited by a large number of literatures and written in many textbooks.

Interestingly, viscosity measurements of neutral polymer solutions were also found that the reduced viscosity deviated from the Huggins equation and could not meet the linear dependence between reduced viscosity and concentration in the low concentration region. Viscosity curve appeared to be upward or

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downward bending^[6–10]. Cheng *et al.*^[11–14] systematically studied the abnormal viscosity behaviors of neutral polymers in extremely dilute solutions, and confirmed that those phenomena were ascribed to interfacial effect. The upward bending was caused by adsorption which occurred in the capillary viscometer in the process of viscosity measurements, while the downward bending was due to transition of flow mode from the viscous flow to slip flow. According to this theory, through analyzing the viscosity data of dilute polymer solutions, structural information of polymers in solution and at capillary wall could be obtained. This was undoubtedly a motivational effect on accurate understanding various issues such as the pathogenesis of cardiovascular disease and so on.

On the basis of aforementioned works, the abnormal viscosity behaviors of polyelectrolytes in dilute solution have been studied. In this work, the viscosity data of the derivatives of poly-2-vinylpyridine reported by previous researchers^[15] have been reviewed. Then, the molecular weight dependence of the abnormal viscosity behaviors of polyelectrolytes has been also investigated for a series of sodium polystyrene sulfonate samples. It was found that the viscosity behaviors of polyelectrolytes were well described by the new proposal theory, and the nature of “polyelectrolyte effect” was ascribed to the interface effect.

THEORETICAL MODEL

Cheng *et al.* corrected the apparent relative viscosity data from Einstein viscosity equation based on the interface effect on polymer viscosity measurement of dilute solution with the Langmuir adsorption model. A quantitative expression to describe experimental viscosity ($\eta_{r, \text{exp}}$) and true viscosity ($\eta_{r, \text{true}}$) is shown below^[16]:

$$\eta_{r, \text{exp}} = \eta_{r, \text{true}} \cdot \left[1 + \frac{k \cdot c}{c_a + c} \right] \quad (1)$$

$\left[1 + \frac{k \cdot c}{c_a + c} \right]$ is expressed as the contribution to relative viscosity of polymer solutions. c_a is the concentration at which half of the active sites of the viscometer capillary wall surface was adsorbed by the polymer. k is a parameter related to the adsorption layer thickness, where k is positive for the adsorption model; k is negative, and $c_a = 0$ for the slip flow model^[11–14]. Effective thickness of the adsorbed layer (b_{eff}) can be evaluated from the parameter k coupled with the known capillary radius R :

$$b_{\text{eff}} = R \cdot \left[1 - \frac{1}{(1+k)^{1/4}} \right] \quad (2)$$

Furthermore, according to Cluster theory^[17], true relative viscosity of polymer solution can be expressed as:

$$\eta_{r, \text{true}} = 1 + [\eta] \cdot c + 6 \cdot K_M \cdot [\eta] \cdot c^2 \quad (3)$$

and

$$\frac{\eta_{\text{sp}}}{c} = [\eta] + 6 \cdot K_M \cdot [\eta] \cdot c \quad (4)$$

where K_M is the molar self-association constant. Based on Eq. (4) and traditional Huggins viscosity equation, the dimensionless Huggins constant K_H can be expressed below:

$$K_M = \frac{K_H \cdot [\eta]}{6} \quad (5)$$

However, the physical meanings of K_M and K_H are quite different. The Huggins slope constant is dimensionless, while the molar self-association constant of K_M reveals the tendency of inter-chain cohesion due to chain penetration in solution, by which the dynamic contact concentration proposed by Qian^[18] can be evaluated.

The experimental relative viscosity can be deduced from Eqs. (1) and (3):

$$\eta_{r,\text{exp}} = (1 + [\eta] \cdot c + 6 \cdot K_M \cdot [\eta] \cdot c^2) \cdot (1 + k \cdot \frac{c}{c_a + c}) \quad (6)$$

The inter-chain aggregations of polyelectrolyte are absent in the dilute solution because of the coulomb repulsion force, which results in $K_M = 0$, therefore, Eq. (6) can be further simplified as

$$\eta_{r,\text{exp}} = (1 + [\eta] \cdot c) \cdot \left[1 + \frac{k \cdot c}{c_a + c} \right] \quad (7)$$

The reduced viscosity can be expressed as:

$$\frac{\eta_{sp}}{c} = \frac{(1 + [\eta] \cdot c) \cdot \left[1 + \frac{k \cdot c}{c_a + c} \right] - 1}{c} \quad (8)$$

From Eqs. (7) and (8), the viscosity behaviors of polyelectrolyte in dilute solution can be described only by three parameters ($[\eta]$, k , and c_a), which reflect the structural state of polymer in solution and at the capillary wall, respectively. Based on this theory, we have reviewed the previous viscosity data of derivatives of poly-2-vinylpyridine reported by Maclay and Fuoss^[15], and studied the abnormal viscosity behaviors of a series of sodium polystyrene sulfonate samples in dilute aqueous solutions, respectively.

MATERIALS AND METHODS

Reagents

Styrene (C.P.) was purchased from Huakang Biotech Ltd. (Nanjing, China) and purified by vacuum distillation before use. Initiator *n*-BuLi was prepared in our laboratory. Other reagents were all A.R. grade without further purification before use. The deionized water was used in all experiments.

Sodium polystyrene sulfonate (NaPSS) was synthesized from a series of polystyrene (PS) samples with narrow molecular weight distribution, which were obtained by anionic polymerization using *n*-BuLi as initiator. The molecular weights of PS were measured by size exclusion chromatography (SEC) which was performed at room temperature on a Waters Associates SEC model 210 equipped with a refractive index detector Model 440. The set of column was including μ -StyragelTM 10³, 10⁴ and 10⁵ nm (Waters Assoc.). HPLC grade THF was used as eluent at a flow rate of 1 mL/min. The molecular weights of various samples were calculated from the relation curve of molecular weights of polystyrene standard samples upon eluent time. Then, the sulfonated polystyrene samples were prepared through sulfonation reaction, then neutralized by NaOH aqueous solutions. The sulfonation degree (DS) was determined by ¹H-NMR spectroscopy. Detailed parameters of various polystyrene and sodium polystyrene sulfonate samples are all listed in Table 1.

Table 1. Specific parameters of various polystyrene and sodium polystyrene sulfonate samples

Polystyrene	$M_n \times 10^{-4}$	d	Sulfonation degree, DS (%)	$M_n(\text{NaPSS}) \times 10^{-4}$ *
1	44	1.25	96	85.4
2	21	1.26	90	39.5
3	10.7	1.01	102	21.4
4	4.5	1.10	100	8.9
5	2.6	1.03	92	4.9

$$* M_{\text{NaPSS}} = \frac{M_{\text{PS}}}{104.15} \times \left[104.15 + \frac{DS}{100} (120.06 - 18.02) \right]$$

Viscosity Measurements

All viscosity measurements were carried out with a Ubbelohde-type glass viscometer with the diameter of

0.40 mm. First, it was soaked in a chromic acid mixture for one day, then rinsed with boiled deionized water under ultrasonic vibrations. At last, the clean glass viscometer was dried in a common oven at 80°C.

A stock solution with accurate concentration 0.5% (*W/W*) was freshly prepared at room temperature. A known weight of solvent was transferred into the viscometer, and its efflux time t_v was measured carefully. Then, a definite amount of stock sample solution with known weight concentration was added into the viscometer by successive weighing until the relative viscosity reached a predetermined point. This was performed to increase the solution concentration in the viscometer. The efflux time t_i for each solution with different concentrations in the viscometer was measured. The ratio of flow time of solution to that of solvent, t_i/t_v , was regarded as the relative viscosity. Because the concentration of solution under test was extremely dilute, the obtained weight concentration of the solution (g/g) was converted to the weight-volume concentration (g/mL) approximatively. All viscosity experiments were carried out in a precise thermostat bath (JWC-52 type, Sierda Scientific Instruments Co., Ltd. Shanghai, China), and the control accuracy was $\pm 0.01^\circ\text{C}$.

RESULT AND DISCUSSION

Derivatives of Poly-2-vinylpyridine

Maclay and Fuoss^[15] prepared polyelectrolytes by partial quaternization of poly-2-vinylpyridine with methyl and *n*-butyl bromide, respectively. It was found that the former salt in water and methanol and the latter in water, methanol, ethanol and nitro methane, showed increase of reduced viscosity upon dilution, respectively, the typical “polyelectrolyte effect”, as shown in Fig. 1. It was widely accepted by most researchers as aforementioned that this phenomenon was ascribed to increase of the intra-chain electrostatic repulsion of polymers with decrease of concentration.

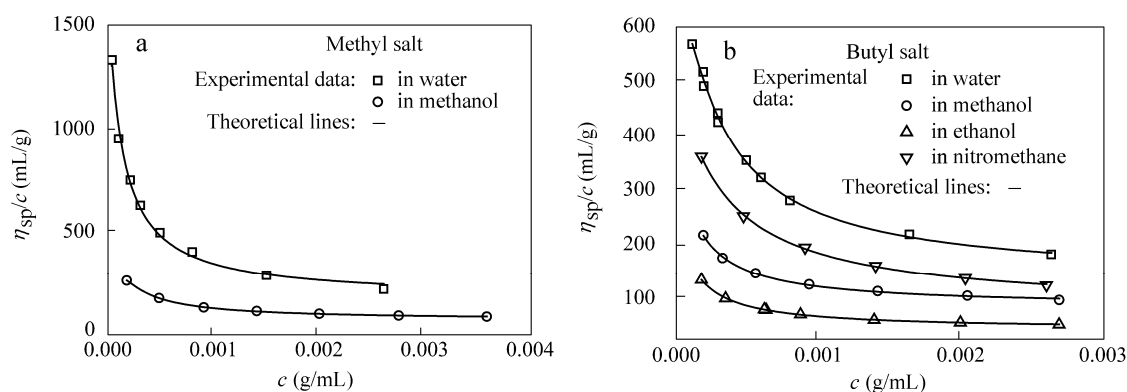


Fig. 1 The plots of reduced viscosities of poly-2-vinyl-*N*-methylpyridinium bromide (a) and poly-2-vinyl-*N*-*n*-butyl pyridinium bromide (b) solutions versus concentrations in various solvents

However, from the theory of interface effect as introduced above, Maclay's and Fuoss' data were tried to be fitted according to Eq. (8) through “non-linear curve fit” in software of Origin 6.0, as shown in Fig. 1 also. It could be seen that the experimental data points were consistent with the theoretical lines very well, which indicated that the upward bending of reduced viscosities may be due to polymer adsorption on the capillary wall. As was known, the glass capillary wall contained a large number of Si—OHs which were facile to interact with the polar groups on the polymer backbone, and polyelectrolytes were available to adsorb on the glass surface. Furthermore, parameters of $[\eta]$, k , and c_a for the derivatives of poly-2-vinylpyridine in various solvents could be obtained from the fitting results and summarized in Table 2. According to Eq. (2), the ratio of the effective adsorption thickness b_{eff} to the capillary radius (R) was calculated and listed in Table 2 also. The normalized ratios of b_{eff}/R was instead of b_{eff} for further comparison. It was found that the relevant parameters were different in various solvents. It was well known that the conformational status of a macromolecule in solution depended

primarily on two kinds of molecular interactions: polymer segment-solvent and polymer segment-segment interactions. The competition of the two kinds of interactions resulted in various conformations of polymer chains in solutions. The different solvents had different interactions with polymers, which caused various conformations of polymers and different resultant parameters of $[\eta]$, k , and c_a as showed in Table 2.

Table 2. Summary of viscosity parameters of the derivatives of poly-2-vinylpyridine in various solvents

Polymer	Solvent	$[\eta]$ (mL/g)	c_a (g/mL)	k	b_{eff}/R
Methyl salt	Water	118.6	0.000149	0.224	0.0493
	Methanol	62.9	0.000201	0.075	0.0179
Butyl salt	Water	96.4	0.000310	0.197	0.0440
	Methanol	74.8	0.000214	0.055	0.0133
	Ethanol	41.2	0.000130	0.028	0.0069
	Nitromethane	65.5	0.000335	0.149	0.0341

Moreover, Maclay and Fuoss also fitted their data according to an empirical formula^[19], which was shown in Eq. (9).

$$\frac{\eta_{\text{sp}}}{c} = \frac{A}{(1 + B\sqrt{C})} + D \quad (9)$$

Where A , B and D are the relevant parameters, based on the definition of intrinsic viscosity ($[\eta]$), $[\eta]$ is deduced from Eq. (9):

$$[\eta] = \frac{\eta_{\text{sp}}}{c_{c \rightarrow 0}} = A + D \quad (10)$$

From the fitting results, the experimental data were also consistent with the theoretical lines well, but the values of parameter A obtained by extrapolation in various solvents were mostly infinite^[15]. Based on Eq. (10), most of $[\eta]$ were also infinite and could not be obtained, which indicated that the Fuoss empirical formula was unreasonable. However, from the viewpoint of interface effect, the model not only fitted the experimental data on phenomenology very well, but also gave unambiguous physical meaning of every parameter and reasonable values including $[\eta]$, k , c_a , and b_{eff} , which further indicated that the theoretical model based on interface effect was proper to polyelectrolytes.

Sodium Polystyrene Sulfonate (NaPSS)

As mentioned above, the derivatives poly-2-vinylpyridine are a class of cationic polyelectrolytes, and the applicability of the theoretical model was also tried to sodium polystyrene sulfonate (NaPSS), a class of anionic polyelectrolytes. The various NaPSS samples were prepared by adjusting reaction conditions. The detailed informations of these samples were presented in Table 1, and it was found that the sulfonation degree of various NaPSS was roughly similar and ranged between 90% and 102%.

The concentration dependence of measured reduced viscosities of various NaPSS samples in aqueous solutions was shown in Fig. 2. It was found that NaPSS had similar viscosity behaviors to those of the derivatives of poly-2-vinylpyridine: the reduced viscosities increased as concentration decreased. Then, the experimental data were also fitted according to Eq. (8) as shown in Fig. 2. It could be found that the theoretical fitting curves as thin solid lines fitted the experimental data in a fairly good way, which indicated that the theoretical model based on interface effect was suitable to describe the viscosity behaviors of various NaPSS samples in aqueous solutions, and the abnormal viscosities were caused by the solute adsorption on the capillary wall. With combination of the derivatives of poly-2-vinylpyridine as mentioned above, it was considered that both positively and negatively charged chains could be adsorbed on the glass capillary wall, which was mainly ascribed to the intermolecular interactions between polymer chains and Si—OH groups, not electrostatic interactions. More detailed investigations will be done in the future work.

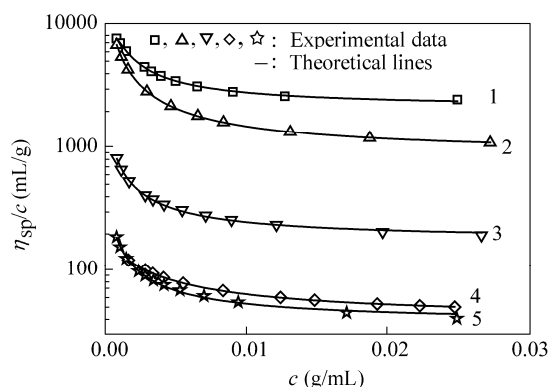


Fig. 2 The plots of reduced viscosities of various NaPSS aqueous solutions versus concentration

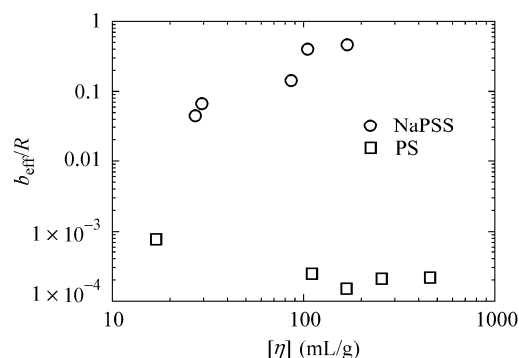


Fig. 3 The plots of the ratio b_{eff}/R of PS ($\square$) and NaPSS ($\circ$) samples versus the intrinsic viscosity, respectively

Meanwhile, the relevant parameters of NaPSS obtained from theoretical fitting are listed in Table 3. Combined with the results in Table 1, it was found that $[\eta]$, reflecting the hydrodynamic volume of polymer single chain in an extremely dilute solution, increased with the molecular weight of NaPSS increase, which was ascribed to the fact that higher molecular weight of a certain polymer had larger hydrodynamic volume in the same solvent. From Table 3, it was interesting that parameters k , reflecting the degree of adsorption, also increased with the molecular weight increase, and effective thickness of the adsorbed layer (b_{eff}) calculated by Eq. (2) showed similar molecular weight dependence on k . However, c_a had no regular dependence, which may be due to the fact that the conformation of polymer chains in solution was influenced by not only the molecular weight but also the sulfonation degree of samples. From Table 1, there still existed some difference in the sulfonation degree among various NaPSS samples.

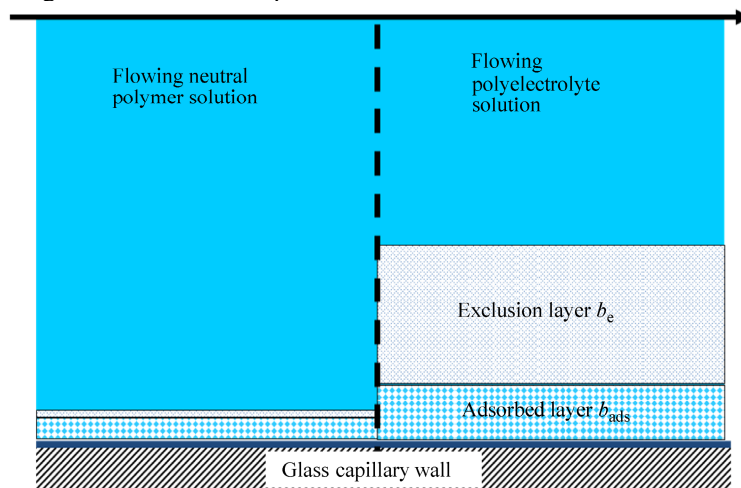


Fig. 4 Schematic presentation for the interface effects of polyelectrolyte and neutral polymer solutions in the capillary flow

Table 3. Summary of viscosity parameters of various NaPSS in aqueous solutions

NaPSS	$[\eta]$ (mL/g)	c_a (g/mL)	k	b_{eff}/R
1	170.0	0.00105	10.54	0.457
2	106.0	0.00061	6.931	0.404
3	87.0	0.00080	0.873	0.145
4	29.4	0.00229	0.310	0.065
5	27.2	0.00086	0.199	0.044

Furthermore, from the numerical value of NaPSS, b_{eff} was much greater than the thickness of absorbed layer of its precursor neutral polystyrene (PS)^[20] as shown in Fig. 3. With regard to polyelectrolyte adsorption at the capillary wall, in addition to the swollen adsorbed solute layer (b_{ads}), there still existed an electrostatic exclusion layer (b_e), which was generally much larger than b_{ads} . The calculated b_{eff} comprised b_{ads} and b_e , *i.e.* b_{eff} was equal to the sum of b_{ads} and b_e , as shown in Fig. 4.

Therefore, b_{eff} of polyelectrolytes was much larger than that of neutral polymers. In addition, for higher molecular weight samples, b_{ads} as well as b_e was apparently larger, so b_{eff} increased with the molecular weight of sample increase, correspondingly.

CONCLUSIONS

In summary, based on systematic study on viscosity behaviors of derivatives of poly-2-vinylpyridine and a series of sodium polystyrene sulfonate samples, the nature of “polyelectrolyte effect” could be ascribed to interface effect in viscous capillary flow. The viscosity behaviors of dilute polyelectrolyte solutions were described only by three parameters ($[\eta]$, k , and c_a), which reflected the structural state of polymer in solution and at the capillary wall, respectively. According to this theory, the structure of polymers in solution and at the interface of glass capillary could be explored by studying their viscosity behaviors in dilute solutions.

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