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Theoretical calculation of reduced viscosity of polyelectrolyte solutions

Koji Nishida, Keisuke Kaji*, Toshiji Kanaya

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611-0011, Japan

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Abstract

Intermolecular electrostatic interactions of polyions contributing to the reduced viscosity are calculated for two molecular models of charged points and skewed rods. These simplified models approximately describe inter-polyion configurations in the actual polyelectrolyte solutions to qualitatively reproduce the characteristic peak of the reduced viscosity appearing at lower concentrations. The long-standing theoretical equation by Rice and Kirkwood was adopted for this calculation because of its simplicity. For the potential term of this equation, we assumed a Debye type screening potential as a function of ionic strength. The results show that the skewed rods model well fits with the experimental data. Furthermore, it should be pointed out that the configurations of this model correspond to the basic constituents of the so-called isotropic model proposed by de Gennes et al. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reduced viscosity; Polyelectrolyte; Coulomb potential

1. Introduction

In the case of neutral polymer solutions, the reduced viscosity η_{SP}/C is proportional to the concentration C in the dilute solution. This well-known relation is used for determining the intrinsic viscosity $[\eta]$ simply by extrapolating to $C = 0$. On the other hand, the reduced viscosity of the salt-free polyelectrolyte solution exhibits an anomalous behavior; it increases with decreasing C and in a range of very dilute concentrations such as 10^{-5}–10^{-4} mol/l, it shows an intense maximum. Such behavior makes it difficult to extrapolate η_{SP}/C to $C = 0$ for determining $[\eta]$ of the polyelectrolyte solution. Therefore, it is of great importance to clarify the cause for this characteristic behavior quantitatively, and to indicate how to obtain $[\eta]$. In this paper, we concentrate on solving this problem, and in a subsequent paper, as an application of this result, we will show how to decompose the reduced viscosity η_{SP}/C at finite concentrations into its intermolecular η_{inter}/C part and intramolecular η_{intra}/C part as a function of concentration.

In most textbooks [1] and literature [2], the increase of the reduced viscosity of polyelectrolyte solutions with dilution has been ascribed to the expansion effect of polyion chains. This effect was formerly explained as follows. When the polymer concentration is high, the intramolecular electrostatic repulsive forces of polyions are greatly screened by counterions, resulting that the polyion chains assume conformations similar to neutral polymers. As the polymer concentration decreases, the screening effect of counterions becomes weaker and weaker, then the polyion chains expand more and more due to the rise of the intramolecular repulsive forces. Consequently, the reduced viscosity of the polyelectrolyte solution increases with dilution. However, this idea does not explain the reason why η_{SP}/C has a maximum value. Of course, the expansion effect of polyion chains must contribute more or less to η_{SP}/C, but it should increase η_{SP}/C monotonously with dilution, and after the complete extension of polyion chains, the reduced viscosity would be constant.

An alternative explanation for this characteristic behavior was suggested by Eisenberg and Pouyet [3] in terms of the intermolecular electrostatic interaction between polyions. They observed that in spite of the strong decrease of the maximum value of η_{SP}/C with increasing the added salt concentration C_s, $[\eta]$ is relatively slightly affected by the increase of C_s and considered that this observation is an evidence for the contribution of the intermolecular electrostatic interaction. In other words, the addition of a small amount of salt greatly shields the intermolecular (long-range) interaction, but it only slightly affects the intramolecular (short-range) interaction. Another possible explanation is the electroviscous effect [4] due to the interaction between a polyion and counterions, namely, the effect of distortion of the counterion layer around the

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* Corresponding author. Tel.: +81-774-38-3140; fax: +81-774-38-3146.
E-mail address: kkaji@scl.kyoto-u.ac.jp (K. Kaji).

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polyion. These three possible factors affecting the viscosity of polyelectrolyte solutions were reviewed by Wolff [5], but the quantitative contributions of these effects to the viscosity have not so far been obvious.

Recently, Cohen et al. [6] calculated the reduced viscosity of the polyelectrolyte solution by applying the mode–mode coupling approximation [7] to the hydrodynamics of charged Brownian spheres in reciprocal space and succeeded in explaining the characteristic feature of η_{SP}/C vs. C for polyelectrolyte solutions qualitatively. In their calculation, the electrostatic repulsive potential between polyions is essential. Similar treatments were reported by Borsali et al. [8]. Recent surveys are seen in a review by Föster and Schmidt [9].

In this report, we show the alternative calculation of characteristic curves of the reduced viscosity as a function of C. Our theoretical approach is also based on the interaction between polyions, but the method of calculation is straightforward and understandable. We have derived the reduced viscosity of intermolecular part η_{inter}/C using the statistical relationship between the viscosity and the intermolecular potential given by Rice and Kirkwood [10,11]. In the present derivation, the shielded Coulomb potential between charged points was employed as a first approximation for the intermolecular potential. The calculated relationship, η_{inter}/C vs. C, successfully reproduces the characteristics of the reduced viscosity of polyelectrolyte solutions. This method is so simple to use and gives reasonable results that an application of this method has already been reported [12]. Furthermore, we have improved the model for the intermolecular configuration; we have introduced a 'skewed rods model' from a viewpoint of satisfactorily compromising the real structure and the model simplification. Thus, this improved model can avoid the overestimation of the electrostatic potential in the point-like polyion model where charges are concentrated at points. Another particular advantage of the 'skewed rods model' is that it is applicable to the more concentrated region where the mean spherical approximation never works because of the overlap of the radius of model molecules. Finally, the calculated curves of η_{inter}/C vs. C for these several models will be compared with typical experimental curves of η_{SP}/C vs. C.

2. Intermolecular electrostatic potential

To calculate the intermolecular potential, the number of effective charges per polyion in the solution, Z, is required because in some cases, a part of counterions condense on polyions to reduce the effective charges. According to the condensation theory by Oosawa [13,14] and Manning [15], counterions begin to condense on polyions when the charge density on the polyion exceeds a critical value. Let polyelectrolytes with a contour length L have N charged groups each consisting of a ν_{p} valent ion bonded to the polyion and ν_{c} valent counterions, the counterion condensation criterion is given by

$$\nu_{\mathrm{p}}\nu_{\mathrm{c}}\xi \geq 1, \tag{1}$$

where both ν_{p} and ν_{c} are taken to be positive, ξ is the dimensionless linear charge density on the polyion, called the coupling constant, which is given by $\xi = l_{\mathrm{B}}/a$. Here, $a = L/N$, and l_{B} is the Bjerrum length:

$$l_{\mathrm{B}} = e^2/4\pi\varepsilon kT, \tag{2}$$

e, ε, k and T being the elementary charge unit, the dielectric constant of the solvent, Boltzmann's constant and temperature, respectively. For aqueous solutions, l_{B} is 7.16 Å at 25°C. Then, the fraction of effective charges becomes

$$f = \begin{cases} 1, & \xi \leq (\nu_{\mathrm{p}}\nu_{\mathrm{c}})^{-1}, \\ 1/\nu_{\mathrm{p}}\nu_{\mathrm{c}}\xi, & \xi > (\nu_{\mathrm{p}}\nu_{\mathrm{c}})^{-1}. \end{cases} \tag{3}$$

For a vinyl type of polyelectrolytes, each molecule consisting of P monomers with a monomer length, $a_0 = 2.52$ Å, the linear charge density is given by

$$\xi = (l_{\mathrm{B}}/a_0)\alpha, \tag{4}$$

where α is the fraction of the monomers each having a 1:1 charged group ($\nu_{\mathrm{p}} = \nu_{\mathrm{c}} = 1$). The number of effective charges per polyion is therefore represented by

$$Z = fN = \begin{cases} \alpha P, & \alpha \leq 0.35, \\ 0.35P, & \alpha > 0.35. \end{cases} \tag{5}$$

Furthermore, the intermolecular electrostatic potential $U(r)$ is as well screened with the uncondensed counterions dispersed in the solution. Assuming a Debye type of screening effect, the $U(r)$ for point-like molecules is given by

$$U(r) = [(Ze)^2/4\pi\varepsilon r]\exp(-r/r_{\mathrm{D}}), \tag{6}$$

where r and r_{D} are intermolecular distance and Debye's screening length, respectively. Here r_{D} is a function of total ionic strength I in the solution:

$$r_{\mathrm{D}} = (8\pi l_{\mathrm{B}} I)^{-1/2}. \tag{7}$$

The total ionic strength is given as a sum of concentration $\alpha C/2$ of the uncondensed counterions dissociating from polyelectrolytes, the concentration C_{s} of added salt and the concentration C_{r} of the residual ions in water:

$$I = \begin{cases} \alpha C/2 + C_{\mathrm{s}} + C_{\mathrm{r}}, & \alpha \leq 0.35, \\ 0.35C/2 + C_{\mathrm{s}} + C_{\mathrm{r}}, & \alpha > 0.35. \end{cases} \tag{8}$$

It should be noted that even in the ideal pure water C_{r} is 10^{-7} mol/l because of the dissociated ions of pure water, H^+ and OH^-, and is usually of the order of 10^{-6} mol/l for properly deionized water. When C_{s} is large enough compared with C_{r}, the influence of C_{r} on the screening effect is negligible, while in extremely dilute salt-free solutions, C_{r} plays an important role.

3. Models

At sufficiently dilute concentrations, polyions can be approximated as point-like molecules and then Eq. (6) is applicable. At higher concentrations where the dimension of a polyion is comparable to or greater than intermolecular distance, the point-like approximation may cause some overestimation of intermolecular potential. In order to avoid this problem, we propose the skewed rods model. A similar treatment for the electrostatic interactions between rod-like polyions was reported by Brenner et al. [16]. de Gennes et al. [17] compared the electrostatic energies between rigid rods for several lattice structures, finding that these structures have very similar electrostatic energy. Hence, they proposed the so-called 'isotropic model' for the semidilute regime. This model has been confirmed by several scattering experiments [18–22]. In any lattice model described above, the relative positions between nearest-neighboring rods fundamentally make skew configurations with a skew angle θ between two rods ($0 \leq \theta \leq 90°$) including two extreme cases $\theta = 0°$ (Katchalsky model [23]) and 90°. Based on this concept, we calculated the intermolecular electrostatic potential by arranging two rods in skew positions as shown in Fig. 1. In a more precise representation for the relative configuration between two rods, especially in a dilute system, the φ rotation of the rod in X–Y plane should be taken into consideration, besides the θ rotation in X–Z plane. In this calculation, however, we omit the effect of φ rotation for simplicity since the population for $\varphi > 0°$ may be considered small and the details of the model become less important with decreasing concentration. Here, the distance between the ith charged site on one rod and the jth charged site on the other rod at a given θ is denoted by r_{ij}. Then, the intermolecular potential $U(r, \theta)$ between the rods is assumed to be a simple summation of the screened Coulomb potential between charged sites $u(r_{ij}, \theta)$. Here, it should be noted that $U(r, \theta)$ corresponds to the potential between centers of the rods before averaging over the configuration θ. $U(r, \theta)$ and $u(r_{ij}, \theta)$ are given as follows, respectively:

$$U(r, \theta) = \sum_{i=1}^{Z} \sum_{j=1}^{Z} u(r_{ij}, \theta) \tag{9}$$

and

$$u(r_{ij}, \theta) = [e^2/4\pi\varepsilon r_{ij,\theta}] \exp(-r_{ij,\theta}/r_{\mathrm{D}}). \tag{10}$$

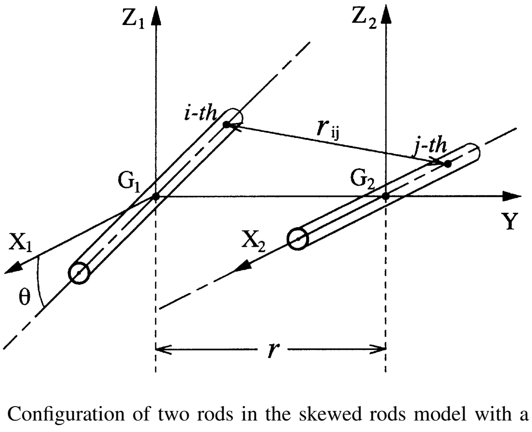

Fig. 1. Configuration of two rods in the skewed rods model with a skew angle θ. r_{ij} and r are the distances between the charged sites and between the centers of mass, respectively.

4. Viscosity of intermolecular part

The contribution of the intermolecular potential to the shear viscosity of simple liquids is given by Rice and Kirkwood [10] as follows:

$$\eta = (M\rho^2/30\zeta) \int_{\mathrm{V}} r^2[(\partial^2 U/\partial r^2) + (4/r)(\partial U/\partial r)]g(r)\,\mathrm{d}r, \tag{11}$$

where M, ρ, ζ and $g(r)$ are mass of a particle, number of particles per unit volume, friction coefficient and radial distribution function of polyions, respectively. In order to perform the integration of Eq. (11) using the intermolecular potential of Eq. (9), the following simplifications and approximations (a)–(c) have been adopted. Although these treatments somewhat lose strictness, they not only provide a tractable way for the practical use, but also give reasonable results. (a) The coefficient of Eq. (11), $1/30\zeta$, is simply taken as an adjustable parameter[1] when we compare with experiment. (b) The radial distribution function $g(r)$ of simple liquid is theoretically given by the following relationship [11]:

$$g(r) = 1 + (8\pi^3\rho)^{-1} \int \mathrm{e}^{\mathrm{i}Q\cdot r}[S(Q) - 1]\,\mathrm{d}Q, \tag{12}$$

where $S(Q)$, Q and r are structure factor, scattering vector and its length, respectively. Here, $S(Q)$ is usually determined by scattering techniques. Practically, it is however very difficult to obtain $g(r)$ experimentally from $S(Q)$, because there are too many kinds of parameters to scan such as, P, C, C_{s} and α, so that we use another expression [24] of $g(r)$ represented by the potential of the mean force $\phi(r)$,

$$g(r) = \exp[-\phi(r)/kT]. \tag{13}$$

For simplicity, we here approximate $\phi(r)$ by the pair

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[1] In the original Rice–Kirkwood theory, ζ is assumed as a friction coefficient of a simple particle with its surrounding particles, which is a constant independent of concentration. In the system of polyelectrolyte solution, it may be considered that the ζ corresponds to a friction coefficient of a polyion with its surrounding media, i.e. mainly solvent, counterions and other polyions. Perhaps, such ζ is not a constant but concentration dependent, since it may be perturbed by the interaction between polyions. Although this problem is another important issue, we here assumed it as a constant. This assumption does not seem to exert a fatal influence, judging from the results.

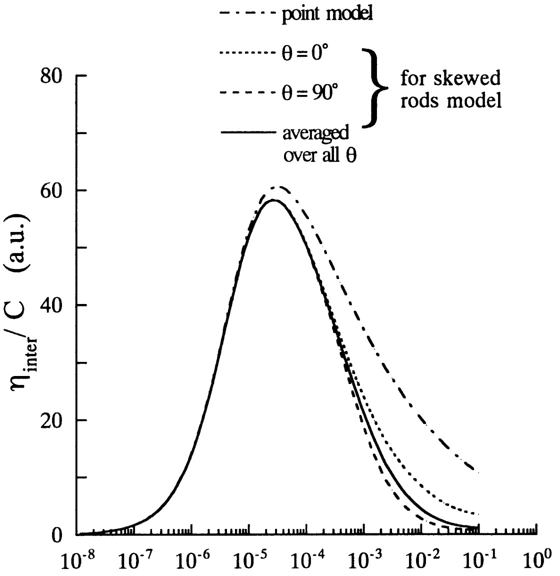

Fig. 2. The comparison among several models in the calculated reduced viscosity due to intermolecular interactions as a function of polyelectrolyte concentration (η_{inter}/C vs. C) for the conditions: $\alpha = 0.35$, $P = 1000$, $C_s + C_r = 1 \times 10^{-6}$ mol/l. (– – –) Point model; (···) skewed rods model at $\theta = 0°$; (- - -) skewed rods model at $\theta = 90°$; (—) skewed rods model averaged over all θ. With regard to the notations, see the text.

potential $U(r, \theta)$ of Eq. (9),

$$g(r, \theta) = \exp[-U(r, \theta)/kT]. \tag{14}$$

In general, this relationship again gives a good approximation [11] for dilute systems, but the quantitative accuracy may somewhat decrease with increasing concentration. In spite of the shortcomings of $g(r)$ function, the integration of Eq. (11) still works because the viscosity is insensitive to the fine structure of $g(r)$. (c) Finally, the configuration-averaged viscosity of intermolecular part η_{inter} can be given as follows:

$$\eta_{\mathrm{inter}} = \int_0^{2\pi} \eta \, \mathrm{d}\theta. \tag{15}$$

In this average, the relative probability that the skew angle is between θ and $\theta + \mathrm{d}\theta$ is weighted by $g(r, \theta)$. For the very dilute region where the distance between the centers of polyions is sufficiently larger than the radius of gyration R_g of the polymer chains ($r \gg R_g$), this procedure would not be necessary.

5. Results of the calculation

Fig. 2 shows the comparison of the calculated reduced viscosity due to the intermolecular part among several models, namely the point-like polyion model and the skewed rods model. For the latter model, two extreme cases of skew positions $\theta = 0$ and 90° and the case of the average over all skew angles are shown. Here, the calculation was carried out under the conditions: $\alpha = 0.35$, $P = 1000$ and $C_s + C_r = 1 \times 10^{-6}$ mol/l for all cases. Every model well reproduces the characteristic peak of the reduced viscosity of typical polyelectrolyte solutions. However, the calculated viscosity due to intermolecular interactions for the point-like polyion model is considerably different from those for the skewed rods model in the higher concentration region. As will be shown later in Fig. 4, the skewed rods model reproduces the observed result of η_{SP}/C vs. C much better than the point-like polyion model, while the difference between the two extreme configurations of the skewed rods model is relatively small. This result is consistent with the concept of de Gennes et al. [17] as was described in Section 3. For a single pair of rods at a given intermolecular distance, of course, the torque acts to twist the rods away from the parallel orientation toward perpendicular configuration [16]; the perpendicular configurations are rather preferred than the parallel orientation. Therefore, more reasonably the viscosity due to intermolecular interactions should be weight-averaged over all skew angles θ, which is taken into account in Eq. (14). Anyhow, as is naturally expected, the difference among these models becomes negligible at sufficiently dilute concentrations.

Fig. 3 shows the calculated curves of η_{inter}/C vs. C as a function of ionic strength of the solvent containing added salt, $C_s + C_r$, using Eqs. (1)–(15). The maximum region in the η_{SP}/C vs. C plot, which is characteristic of polyelectrolyte solutions, is well reproduced. Although Cohen et al. [6] and we independently calculated the reduced viscosity of polyelectrolyte solution due to the intermolecular interaction using different methods, both the results strongly support that the leading term of the characteristic behavior of the reduced viscosity comes from the electrostatic repulsive forces between polyions.

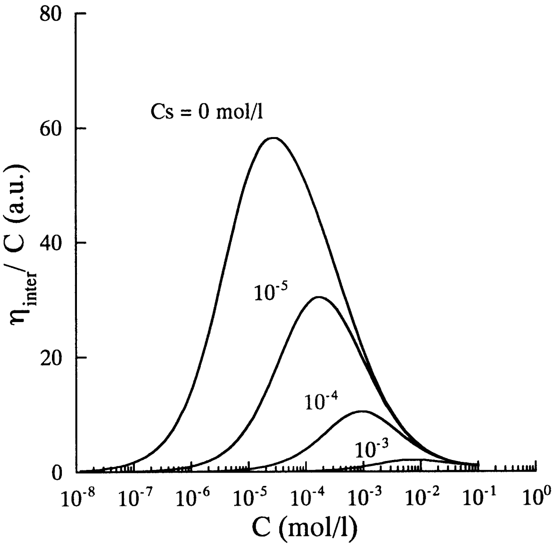

Fig. 3. Intermolecular part of the skew angle-averaged reduced viscosity η_{inter}/C vs. C. The ionic strength of the solvent containing added salt, $C_s + C_r$, is varied from 10^{-7} mol/l (ideal pure water) to 10^{-3} mol/l. The other parameters are the same as in Fig. 2.

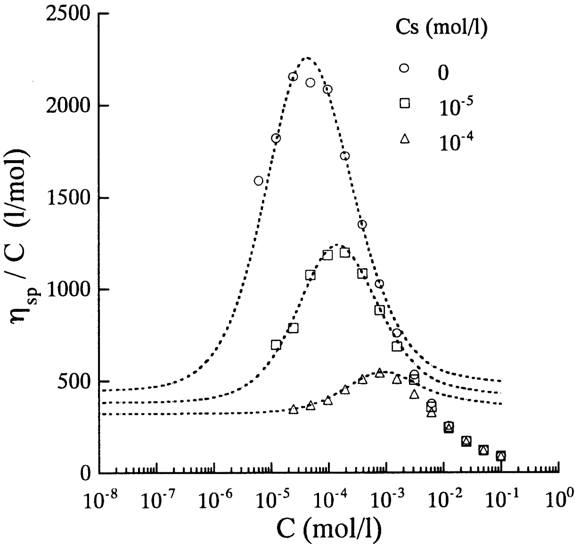

Fig. 4. The observed η_{SP}/C vs. C for sodium salt of partially sulfuric acid–esterified poly(vinyl alcohol) (NaPVS) with $\alpha = 0.31$ and $P \approx 2500$ in added salt solutions. The calculated relations, η_{inter}/C + const vs. C, are also shown by dotted lines, where the same parameters are used as for α and P. (○) $C_s = 0$ mol/l; (□) $C_s = 10^{-5}$ mol/l; (△) $C_s = 10^{-4}$ mol/l.

The increase of η_{inter}/C with dilution in the higher concentration side of the maximum is qualitatively ascribed to the increase of the electrostatic interaction volume ($\sim r_D^3$), whereas the decrease after the maximum is caused by the leveling-off effect of the electrostatic interaction. Therefore, η_{inter}/C for every added salt concentration is asymptotic to a linear function of C in the sufficiently lower concentration range, compared with the concentration at the maximum.

6. Comparison with experiments

Fig. 4 shows the comparison between the calculated and observed reduced viscosity. Here, the samples employed for the experiments were aqueous solutions of sodium salt of partially sulfuric acid–esterified poly(vinyl alcohol) (NaPVS) with $\alpha = 0.31$, $P \approx 2500$ (viscosity-averaged degree of polymerization). Details of the sample preparation were described elsewhere [21]. The calculation was carried out under the same conditions as those of the experiments for α and P. In this figure, it should be noted that the calculated reduced viscosity can well be fit with the observed data in sufficiently dilute regions ($C < 10^{-3}$ mol/l) by assuming the form:

$$\eta_{SP}/C = \text{const} + \eta_{\text{inter}}/C. \tag{16}$$

The constant in Eq. (16) was determined so that the calculated curve would agree well with the observed one at around the maximum position. When $C_s = 0$, the value of C_r was taken as 2.7×10^{-6} mol/l though it was negligible when C_s was not less than 10^{-5} mol/l. This value of C_r corresponds to the ionic strength of deionized water used in this study, which is almost equal to that of 4×10^{-6} mol/l estimated from the pH of the solvent by Cohen et al. [6]. The physical meaning of the 'const' is the hydrodynamic contribution of an isolated chain into the reduced viscosity. Therefore, when the above fitting procedure works well, the parameter 'const' would agree with $[\eta]$ of the polyelectrolyte solution. It is also noticed that the deviation from the relationship of Eq. (16) becomes larger at higher concentrations ($C > 10^{-3}$ mol/l). This is because at such higher concentrations, the conformational contribution cannot be regarded as constant but as a function of polymer concentration C. Recent experimental studies [25,26] have proved that the electrostatic persistence length b_e of a flexible polyelectrolyte chain increases with dilution in a manner, $b_e \sim C^{-1/2}$ for $C > 10^{-2}$ mol/l and then it gradually levels off for $C < 10^{-3}$ mol/l. This can be a good explanation for the deviation mentioned above. Hence, the 'const' in Eq. (16) should be substituted by intramolecular reduced viscosity η_{intra}/C so that it may be applicable to wider concentration range, and the more general expression can be written as follows:

$$\eta_{SP}/C = \eta_{\text{intra}}/C + \eta_{\text{inter}}/C. \tag{17}$$

Further discussion on this issue will be reported in a subsequent paper.

Fig. 5 shows the comparison between the observed and calculated maximum positions $C_{\max}$ in the η_{SP}/C vs. C plot as a function of $C_s + C_r$. As is seen from the figure, the observed $C_{\max}$ approximately agrees with the calculated one. In detail, however, the observed $C_{\max}$ begins to deviate from the calculated value for $C_s + C_r > 10^{-4}$ mol/l. This may be attributable to the conformational change of polyions with increasing C_s. Another noticeable feature of $C_{\max}$ in Fig. 5 is that $C_{\max}$ is almost proportional to C_s in the

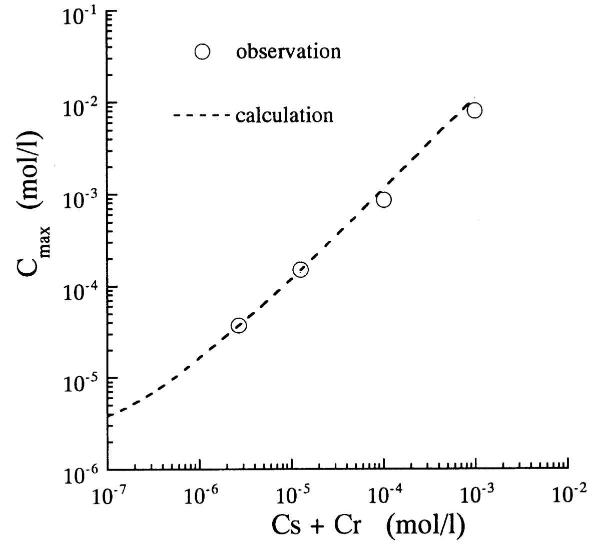

Fig. 5. The plot of the observed and calculated maximum positions $C_{\max}$ against the sum of the added salt concentration and the residual ionic strength, $C_s + C_r$. (○) Observation; (- - -) calculation.

C_s ($\approx C_s + C_r$) range 10^{-5}–10^{-3} mol/l where the slope is almost equal to unity because C_r is negligible in this range. This relation agrees well with the result of Cohen et al. [6]. However, it should be noted again that the additional term C_r is essential for salt-free solutions.

In conclusion, it should be emphasized that the cause for the maximum in the plot of η_{SP}/C vs. C of polyelectrolyte solutions is attributable to the intermolecular electrostatic repulsive potential. When the reduced viscosity of the intermolecular part is calculated, the Rice and Kirkwood's statistical relationship between viscosity and intermolecular potential is very useful. Furthermore, the shielded Coulomb potential for the skewed rods model gives a good approximation as the intermolecular electrostatic potential in polyelectrolyte solutions.

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