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Determination of intrinsic viscosity of polyelectrolyte solutions

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Abstract

Intramolecular hydrodynamic contribution η_{intra}/C to the reduced viscosity η_{SP}/C of polyelectrolyte solutions is derived as a function of polymer concentration C by separating the theoretically calculated intermolecular electrostatic contribution η_{inter}/C from the observed reduced viscosity, assuming an additivity, $\eta_{\text{SP}}/C = \eta_{\text{intra}}/C + \eta_{\text{inter}}/C$. The resulting intramolecular part η_{intra}/C reflects nearly the net effect of the polyion conformation; it increases monotonously with decreasing polymer concentration and levels off to a constant in sufficiently dilute concentrations. The leveling-off value of η_{intra}/C corresponds to the intrinsic viscosity $[\eta]$. From the estimated values of $[\eta]$, the ionic strength I dependence of the polyion conformation has been visualized, resulting in a similarity between two relations, η_{intra}/C vs. C and $[\eta]$ vs. I. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Intrinsic viscosity; Reduced viscosity; Polyelectrolyte

1. Introduction

In discussing the conformation of a single polymer chain from viscometric data, information about the intrinsic viscosity $[\eta]$ is indispensable. Although there are several reports on the intrinsic viscosity of polyelectrolyte solutions [1–7], all these reports were limited to the case where a sufficient amount of salt was added. In salt-free and low added-salt concentration cases, the reduced viscosity η_{SP}/C, C being concentration, of polyelectrolyte solutions exhibits a drastic increase with dilution and an intense maximum appears in a very dilute concentration range (10^{-5}–10^{-4} mol/l) [8–10]. Such a strong peak makes it difficult to extrapolate the reduced viscosity to $C = 0$ and determine $[\eta]$.

In a previous paper [10], we derived the reduced viscosity of intermolecular part η_{inter}/C based on the statistical relationship between viscosity and intermolecular potential given by Rice and Kirkwood [11], where the shielded Coulomb potential and the 'skewed rods approximation' were used. We found that the characteristic features of the reduced viscosity of polyelectrolyte solutions are reproduced in the concentration dependence of the calculated η_{inter}/C vs. C by taking into account the intermolecular electrostatic interactions and that the calculated η_{inter}/C can very well fit in with the observed η_{SP}/C in the very low concentrations by shifting it by a constant. Based on this result, it is possible to separate the reduced viscosity of polyelectrolyte solutions into inter- and intramolecular parts, by assuming the additivity of these two parts in analogy with Huggins equation [12].

In this report, we propose a practical method to derive intramolecular hydrodynamic contribution η_{intra}/C in non-zero concentrations and to obtain $[\eta]$ by extrapolating it. Thus, the intramolecular part of reduced viscosity η_{intra}/C is attempted to calculate as a function of C by subtracting the calculated η_{inter}/C from the experimentally observed η_{SP}/C, and to obtain $[\eta]$ by extrapolating η_{intra}/C to the zero concentration. In order to perform this attempt in the salt-free condition as well as in a wide range of added-salt concentrations C_s, we needed to measure η_{SP}/C to very dilute concentrations. $[\eta]$ is obtained for a wide range of ionic strength I in this way and then it is converted to the persistence length b_t using the Yamakawa–Fujii theory [13].

In Appendix A, we propose a simple empirical relationship between the electrostatic persistence length b_e and the ionic strength I. This empirical equation has been derived by making use of not only the present data but also the data from literature [14–17], and hence, it will be applicable to the usual vinyl-type of polyelectrolytes with monovalent strong acidic groups. For the readers' convenience, in Appendix B we also provide an approximate representation for the η_{inter}/C vs. C relation since the rigorous calculation for this relation is a considerably hard job as was shown in a previous paper [10].

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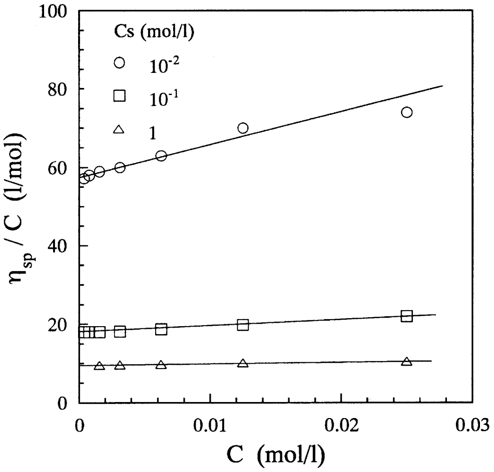

Fig. 1. The observed η_{SP}/C vs. C for NaPVS solution, with $\alpha = 0.31$ and $P = 2500$ in various salt concentrations. (○) $C_s = 10^{-2}$ mol/l; (□) $C_s = 10^{-1}$ mol/l; (△) $C_s = 1$ mol/l.

2. Experimental section

2.1. Materials

Most methods of the preparation and characterization for sodium salt of partially sulfuric acid-esterified poly(vinyl alcohol) NaPVS were previously reported [18]. The NaPVS samples with $\alpha = 0.8$–52% were obtained by changing the reaction condition. The viscosity-averaged molecular weight M_η of a parent PVA was determined to be 110,000 by conventional intrinsic viscosity measurements using the Mark–Houwink–Sakurada equation, where the coefficients for this equation were cited from literature [19]. This value corresponds to a viscosity-averaged degree of polymerization $P_\eta = 2500$. We chose a sample with $\alpha = 31\%$ for the present viscosity study, in order to minimize the number of condensed counterions and maximize the effective charge density. Analytical grade of NaCl was used as added-salt. The parent PVA was kindly presented by Unitika Chemical Co. Ltd (lot no. UV).

2.2. Viscosity measurements

Polyelectrolyte solutions with given concentrations for viscosity measurements were carefully prepared. An Ubbelohde type of capillary viscometer was used for the viscosity measurements. Flow time measurements were conducted in the thermostat at 25 ± 0.01 °C using a laboratory-designed automatic stopwatch system with an optical sensor, which made it possible to measure the time with an accuracy of 10^{-3} s. The capillary inner-surface of the viscometer was washed with a mixed acid of H_2SO_4 and HNO_3 having a ratio of 50:1 and then coated with dimethyl dichlorosilane to prevent the solution from being adsorbed on the glass surface of the capillary. This treatment is particularly important to reduce the dispersion of flow time, which is often caused by droplets adhered on the capillary surface. The atmosphere around the sample solutions was replaced with N_2 gas to prevent the contamination of the solutions with CO_2 acting as added-salt.

3. Results and discussion

Fig. 1 shows the plots of measured reduced viscosity η_{SP}/C for NaPVS solutions as a function of concentration C when highly concentrated salt was added ($C_s = 10^{-2}$–1 mol/l). In the case of such high added-salt concentrations, a linear relationship is approximately observed between η_{SP}/C and C, similarly to the usual non-ionizing polymer solutions, and $[\eta]$ can be easily determined. The obtained value of $[\eta]$ as a function of ionic strength I is shown in Fig. 7 together with the results for low added-salt concentrations.

Fig. 2 shows the plots of η_{SP}/C vs. C for the salt-free case and three low added-salt concentrations. Here a characteristic behavior of the viscosity of polyelectrolyte solutions is observed; η_{SP}/C increases greatly with decreasing C, attaining a maximum at a very low concentration $C = C_{\max}$, and then it goes down. In the concentration regions sufficiently lower than $C_{\max}$, however, η_{SP}/C tends to level off and have a plateau, as is clearly seen in the plots for $C_s = 10^{-3}$ and 10^{-4} mol/l. This fact suggests that the contribution from the polyion conformation itself will remain when the solution is diluted to a concentration where the intermolecular interactions can be neglected. In order to estimate $[\eta]$ of a polyelectrolyte solution by the conventional linear extrapolation, measurements must be conducted to such a very dilute concentration where the reduced viscosity indicates a plateau. For very low $C_s(<10^{-4}$ mol/l), however, it is particularly difficult to perform such measurements and

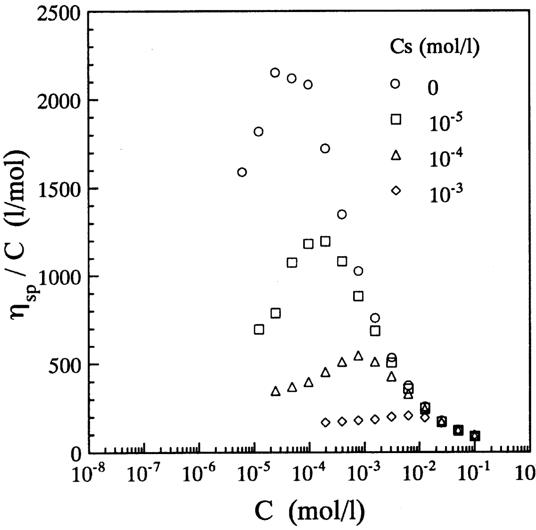

Fig. 2. The observed η_{SP}/C vs. C for NaPVS solution, with $\alpha = 0.31$ and $P = 2500$ in various salt concentrations. (○) $C_s = 0$ mol/l; (□) $C_s = 10^{-5}$ mol/l; (△) $C_s = 10^{-4}$ mol/l; (◇) $C_s = 10^{-3}$ mol/l.

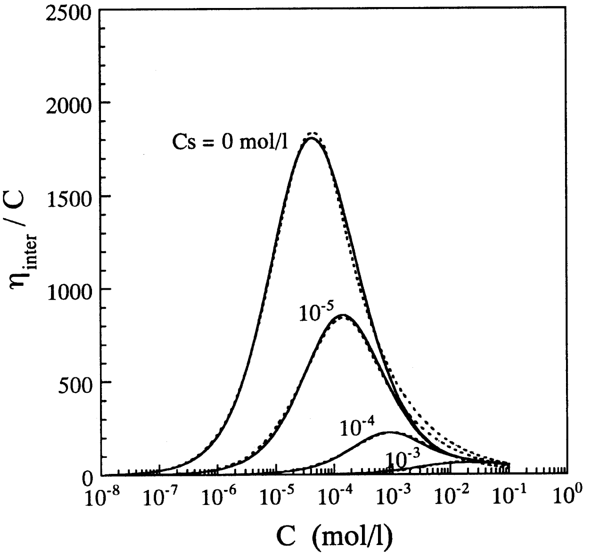

Fig. 3. The calculated intermolecular electrostatic contribution to the reduced viscosity η_{inter}/C vs. C under the same conditions of P, α and C_s as in Fig. 2.

the determination of $[\eta]$ in the salt-free condition has been almost desperate.

As was shown in the previous paper [10], the contribution of the intermolecular potential to the shear viscosity of polyelectrolyte solution without entanglement effects is given as follows:

$$\eta_{\text{inter}} = \langle (M\rho^2/30\zeta) \int_v r^2[(\partial^2 U/\partial r^2) + (4/r)(\partial U/\partial r)]g(r)\,\mathrm{d}r \rangle, \tag{1}$$

where M, ρ, ζ, $g(r)$, and $U(r)$ are mass of a particle, number of particles per unit volume, friction coefficient, radial distribution function of polyions, and intermolecular electrostatic potential, respectively. $\langle\,\rangle$ denotes the average over the relative configurations between polyions; a 'skewed rods approximation' was used in this average procedure. The coefficient of Eq. (1) $1/30\zeta$ was simply taken as an adjustable parameter when the calculation is compared with experimental data.

The solid lines in Fig. 3 show the η_{inter}/C vs. C curves which were theoretically calculated using Eq. (1) under the same conditions for P, α and C_s as in Fig. 2. The details of the method were shown in Ref. [10]. The dotted lines are drawn by using an approximate equation, Eq. (A2), for η_{inter}/C, which is given as a simple and easy method in Appendix B. The maximum in η_{SP}/C vs. C plots, which is characteristic of polyelectrolyte solutions, is reproduced in each calculated curve. η_{inter}/C has a non-zero value even at concentrations less than 10^{-7} mol/l for $C_s = 0$. Thus, the intermolecular electrostatic interaction affects η_{SP}/C even at such dilute concentrations. This fact makes it difficult to get $[\eta]$ for salt-free or low added-salt solutions by simple extrapolation. As was shown in the previous paper [10], the observed reduced viscosity can be fitted with the calculated curve in the sufficiently dilute region ($C < 10^{-3}$ mol/l) by using the form *const* + η_{inter}/C. We can understand this behavior by considering the Huggins equation. In the Huggins equation [12] which usually treats non-ionizing polymer solutions, $[\eta]$ and the higher terms are ascribed to the intramolecular and intermolecular contributions, respectively. In the non-ionizing polymer solutions, the intramolecular contribution is constant and can be taken as $[\eta]$ directly, since the characteristic property of the solvent does not change during the process of dilution and the change in polymer conformation is little expected with dilution. Generally, the reduced viscosity is given by

$$\eta_{\text{SP}}/C = [\eta] + a_1 C + a_2 C^2 + \cdots \tag{2}$$

where a_1 and a_2 are constants. When the concentration is sufficiently dilute and the expansion of polyions is saturated, the η_{SP}/C of polyelectrolyte solutions can be written by analogy with Eq. (2) as

$$\eta_{\text{SP}}/C = [\eta] + \eta_{\text{inter}}/C \qquad (C < 10^{-3}\ \text{mol/l}). \tag{3}$$

However, in a higher concentration range, the polyion conformation is also expected to change with polymer concentration. Then, the intramolecular contribution η_{intra}/C should show a concentration dependence. In the dilute concentration range before the entanglement effect becomes predominant, Eq. (3) can therefore be rewritten as

$$\eta_{\text{SP}}/C = \eta_{\text{intra}}/C + \eta_{\text{inter}}/C. \tag{4}$$

According to this equation, η_{intra}/C can be obtained by subtracting the calculated term η_{inter}/C from the observed reduced viscosity η_{SP}/C. Fig. 4 shows a typical example for indicating the way to separate η_{SP}/C into η_{intra}/C and η_{inter}/C when $C_s = 0$ mol/l; the fitting with the observed data works

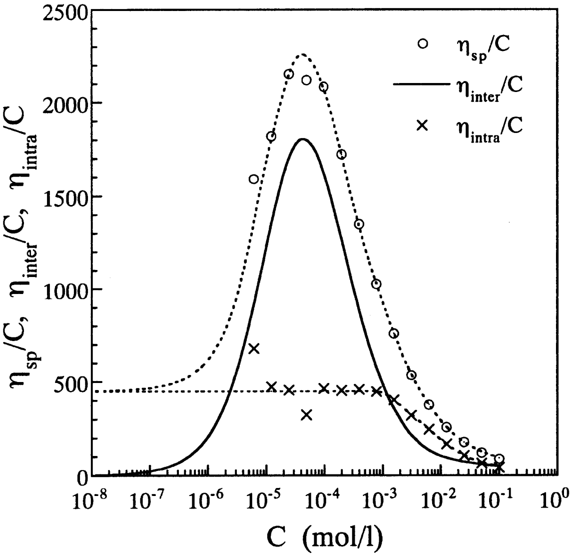

Fig. 4. A typical example for the separation of η_{SP}/C into η_{inter}/C and η_{intra}/C for $P = 2500$, $\alpha = 0.31$, $C_s = 0$ mol/l. (○) observed η_{SP}/C; (—) calculated η_{inter}/C; (×) η_{intra}/C. The dotted lines are guides for the readers' eyes.

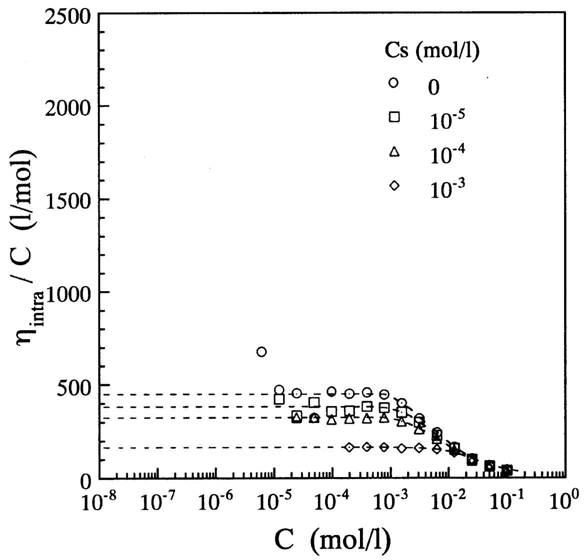

Fig. 5. The intramolecular contribution to the reduced viscosity, η_{intra}/C as a function of C under the same conditions for P, α and C_s as in Fig. 2.

well. Fig. 5 shows the resulting values of η_{intra}/C as a function of C for four different concentrations of added-salt including the salt-free case; the scales are the same as those in Figs. 2 and 3. In Fig. 6 the results for higher added-salt concentrations are shown together with those of Fig. 5 in double logarithmic scales. These results may reflect nearly the net contribution from the hydrodynamic effect of a single polyion as a function of polymer concentration. Therefore, it implies the significant information on the expansion mechanism of a polyion chain. In every added-salt concentration, η_{intra}/C increases with dilution and levels off. The leveling-off concentration decreases with decreasing added-salt concentration. This behavior can be very well explained in terms of the expansion effect of a polyion chain when the intramolecular electrostatic repulsive force is released from the screening effect with decreasing counter ions and added-salt.

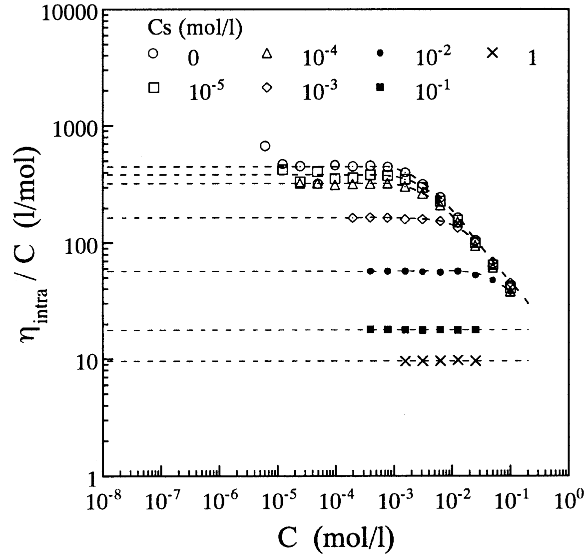

Fig. 6. The intramolecular contribution to the reduced viscosity, η_{intra}/C as a function of C in double logarithmic scales. (○) $C_s = 0$ mol/l; (□) $C_s = 10^{-5}$ mol/l; (△) $C_s = 10^{-4}$ mol/l; (◇) $C_s = 10^{-3}$ mol/l; (●) 10^{-2} mol/l; (■) 10^{-1} mol/l; (×) 1 mol/l.

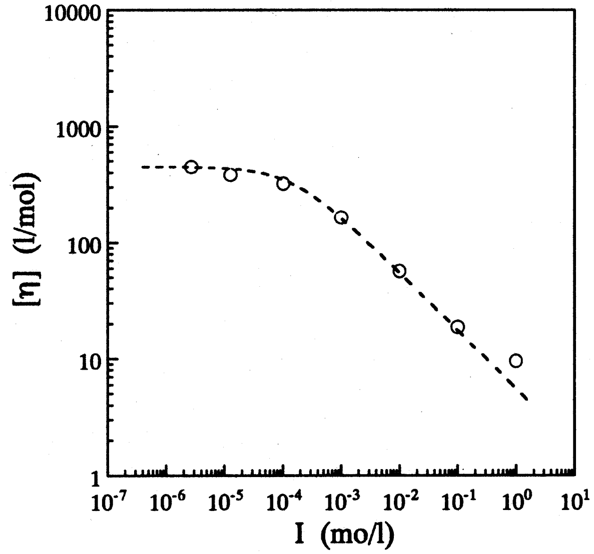

Fig. 7. The intrinsic viscosity $[\eta]$ as a function of ionic strength $I(= C_s + C_r)$ in double logarithmic scales.

The whole characteristic behavior of η_{SP}/C had often been explained by only the expansion effect [20,21], however, the net expansion effect in η_{SP}/C is not so large compared with the intermolecular electrostatic effect [10]. This behavior has been misunderstood for a long time.

Fig. 7 shows $[\eta]$ as a function of $I(= C_s + C_r)$, where C_r is the residual ionic strength of water [10]. For $I \geq 10^{-4}$ mol/l, $[\eta]$ is roughly proportional to $I^{-1/2}$, as was reported in literature [3,7]. However, for $I < 10^{-4}$ mol/l, $[\eta]$ tends to level off, suggesting that the chain expansion due to the intramolecular electrostatic interaction begins to saturate at around this ionic strength. This may be due to the localized higher ionic strength around the polyions [16]. By comparing Figs. 6 and 7, it is seen that the effect of ionic strength I on $[\eta]$ and that of polymer concentration C on η_{intra}/C are in parallel relation. Namely, both added-salt concentration and polyelectrolyte concentration (counter ion concentration) give the same screening effect.

The chain expansion effect in terms of persistence length is discussed later. In the following treatment, it is assumed that the expansion of a polyion is caused by only the increase in electrostatic persistence length, i.e. the excluded volume effect is neglected. However, it should be noticed that the electrostatic excluded volume effect possibly contributes to the expansion of a polyion. Therefore, the persistence length obtained by the following treatment is somewhat apparent and is an upper limit of the true persistence length [22]. The present authors consider that this effect is not serious because the persistence lengths obtained

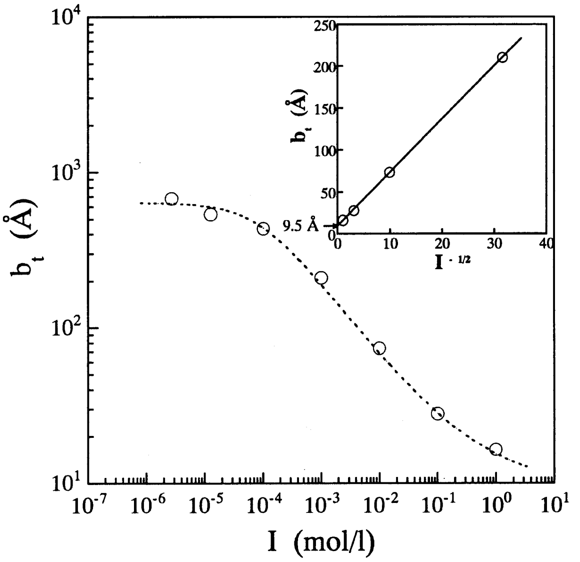

Fig. 8. The persistence length b_t as a function of ionic strength $I(= C_s + C_r)$ in double logarithmic scales. The insertion shows $I^{-1/2}$ dependence of the persistence length b_t.

from neutron scattering (NS) experiments, which directly give true persistence lengths, almost agree with those from the viscosity data within experimental error. Though the NS data is limited within intermediate concentrations, the excluded volume effect can be considered to decrease with approaching stretched conformation in the lower ionic strength. Within the framework mentioned above, the persistence length b_t can be obtained from the intrinsic viscosity $[\eta]$ with the contour length L and the diameter of cross-section d of polyion using Yamakawa–Fujii theory [13]. Here, L is assumed as $a_0 P_\eta$, where a_0 is monomer length, and d was determined to be 8 Å from a small-angle X-ray scattering data [18] for the identical sample with that of the present study, following the previously reported method [23]. Fig. 8 shows the ionic strength I dependence of the persistence length b_t. As seen from this figure, the persistence length b_t of the flexible polyion chain widely changes with I, covering almost two orders of magnitude. However, as also seen from this figure, the increase of b_t tends to level off at around $I = 10^{-4}$ mol/l similarly to the case of $[\eta]$. Therefore, flexible polyelectrolyte chain cannot extend infinitely, contradicting the old assumption [24]. The electrostatic contribution to the total persistence length is estimated by subtracting the intrinsic persistence length b_0 of the polyion chain [17]. The intrinsic persistence length b_0 is estimated by extrapolating b_t to the infinitely large ionic strength. The insertion in Fig. 8 shows an $I^{-1/2}$ dependence of the persistence length b_t, and the value of the intercept with the b_t axis gives $b_0 = 9.5$ Å. Then, the electrostatic persistence length b_e is obtained by the following relation:

$$b_e = b_t - b_0. \tag{5}$$

The resulting b_e together with the values from literature is shown in Fig. 9. This empirical relation can be represented by Eq. (A1) in Appendix A in good approximation.

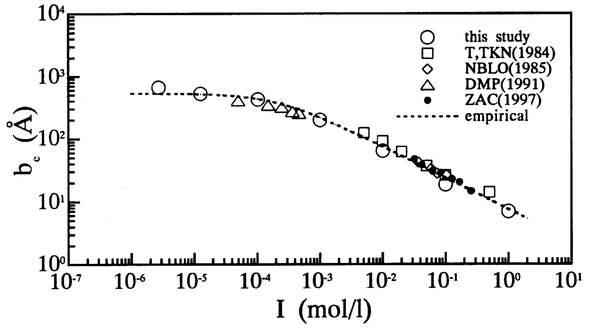

Fig. 9. The electrostatic persistence length b_e as a function of ionic strength $I(= C_s + C_r)$ in double logarithmic scales. (○) this study; (△) transient electric birefringence by Degiorgio et al. [14]; (□) intrinsic viscosity by Tricot [15] and Takahashi et al. [5]; (●) SANS by Nishida et al. [16]; (◇) SANS by Nierlich et al. [17].

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Appendix A. Empirical master curve of the electrostatic persistence length

We have shown a tractable method to obtain the intrinsic viscosity $[\eta]$ of polyelectrolyte solution. The estimation of the accuracy of this method is difficult especially for the salt-free case because it is a unique method. Therefore, we will compare the values of b_e obtained by the present method with that from literature. Fig. 9 shows the ionic strength I dependence of the electrostatic persistence length b_e of the present study (○) and from literature [14–17]. Fairly good agreement is found between the present data and the data by Degiorgio et al. (△) [14] including a value for the lowest ionic strengths reported so far. Because of the experimental difficulty in the determination of b_e the data points are dispersed with an extent of 20%. However, an empirical master curve can be found by surveying a greatly wide region. The dotted curve is drawn so as to best reproduce the general feature of the I dependence of b_e in the wide I range. As the master curve for the observed data, we propose the following relationship between b_e and I

$$b_e = 7.5(I + 2 \times 10^{-4})^{-1/2}, \tag{A1}$$

where the units of b_e and I are Å and mol/l, respectively. This empirical equation, of course, potentially implies an error of the same extent of the dispersion of data based upon and it should be improved by making full use of forthcoming major data.

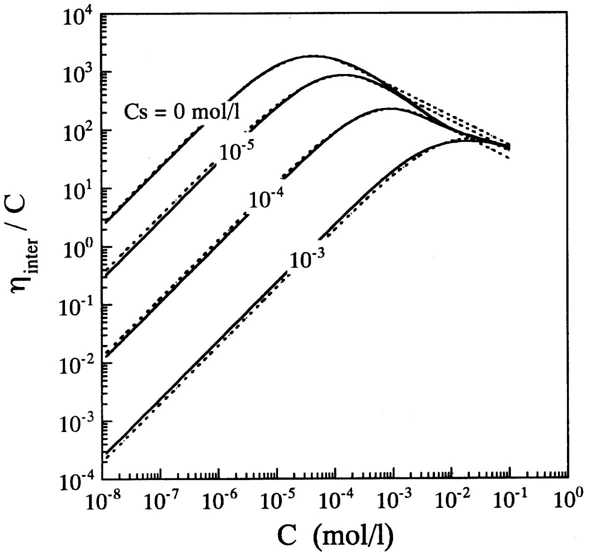

Fig. 10. The calculated intermolecular electrostatic contribution to the reduced viscosity η_{inter}/C vs. C using Eq. (1) (solid lines) and their approximated representation using Eq. (A2) (dotted lines). Other conditions are the same as in Fig. 2.

Appendix B. Approximate representation of η_{inter}/C

The physical meaning of the intermolecular contribution to the reduced viscosity and the method for the rigorous calculation of η_{inter}/C vs. C were described in the previous paper [10], however, it is quite bothersome to calculate such curves corresponding to various conditions of actual measurements. Therefore, we provide an approximate representation of the η_{inter}/C vs. C relation for the readers' convenience. The solid lines in Fig. 10 show the theoretically calculated curves for η_{inter}/C vs. C in double logarithmic scales using Eq. (1) under the same conditions for P, α and C_s as those in Fig. 2. These curves are accompanied by two asymptotic lines. In the lower concentration side of the maximum position C_{max}, η_{inter}/C is proportional to C while in the higher concentration side, η_{inter}/C is roughly proportional to $C^{-1/2}$. Both of the asymptotic lines level off at around $C = C_{max}$. Taking these behaviors into consideration, an approximate equation is derived as follows

$$\eta_{inter}/C \approx A_1[1 - \exp(-0.17C/A_2)][(C + A_2)/A_2]^{-1/2}, \quad \text{(A2)}$$

which fairly well reproduces the rigorously calculated curves of η_{inter}/C vs C. Here A_1 is a simple adjustable parameter and A_2 is a parameter having a value near to $C_s + C_r$. The dotted lines in Fig. 10 are drawn by using this approximate equation. In higher concentrations the approximation becomes rather poor, but in the actual application, this deviation is not so serious when the fitting of η_{SP}/C with $[\eta] + \eta_{inter}/C$ is conducted for $C < 10^{-3}$ mol/l.

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