

alent when eq. 8 is employed where $C_c = C_h$. However, eq. 8 may have the added utility of providing a means of assessing the size of a "denaturing unit," given by the magnitude of N required to fit the data when $C_c \neq C_h$.

Acknowledgments.—The authors wish to thank Dr. Milton Noelken for performing the optical rotatory dispersion measurements, Dr. Elkan Blout for graciously providing a sample of poly-L-glutamic acid, and Profes-

sors E. Peter Geiduschek and Charles Tanford for enlightening discussions. We also wish to express our gratitude to Professor Stuart Rice for educating us on the proper choice of standard state for free electrons in aqueous solution.

We gratefully acknowledge a discussion with Mr. Roland Hawkins, which gave us a better understanding of the content of ref. 18. The ideas in Appendix I resulted from the insight thus provided.

(CONTRIBUTION FROM THE DEPARTMENTS OF APPLIED CHEMISTRY AND SYNTHETIC CHEMISTRY, NAGOYA UNIVERSITY, FURO-CHO, CHIKUSA-KU, NAGOYA, JAPAN)

Excluded Volume of Polyelectrolyte in Salt Solutions

BY AKIRA TAKAHASHI AND MITSURU NAGASAWA

RECEIVED JULY 15, 1963

The intrinsic viscosities of sodium poly-(acrylate) having different molecular weights were determined in sodium bromide solutions of various concentrations. The analysis of the data was based on three different theories; Flory and Fox; Kurata, Stockmayer, and Roig; Stockmayer and Fixman. Both K. S. R. and S. F. plots converged at one point, respectively, with different concentrations of sodium bromide, as those theories predicted, whereas F. F. plots did not give the same intercept against the prediction of the theory. From the slopes of K. S. R. and S. F. plots, the mutual excluded volume of segments was determined. The values obtained were compared with the values calculated using the Debye-Hückel theory for the potential of average force between two segments. Large disagreement was observed between the experimental and calculated results, and, moreover, the mutual excluded volume was found to be proportional to the inverse root of sodium bromide concentration, while the calculated result predicts its proportionality to the inverse of sodium bromide concentration. The reason for the discrepancy between theory and experiment is considered to be due to neglect of the counter-ion effect in calculating the mutual excluded volume.

Introduction

During the past 15 years, great efforts have been devoted to clarify the well known expansion problem of a linear poly-ion in solution both theoretically and experimentally.¹ The origin of the molecular expansion is now accepted to be the electrostatic repulsive force among fixed charges on the polyion. Owing to the electrostatic repulsion between fixed charged groups, the molecular dimension of the poly-ion increases to several times as large as that of the original uncharged polymer and varies markedly with the concentration of added neutral salt, *i.e.*, with ionic strength of solution.

In spite of so many papers published to compute the problem quantitatively, there is still great disagreement between theories and experimental results. In all cases, the calculated expansions of the poly-ion are much larger than the experimental ones if we use the analytical charge density of poly-ion to calculate the repulsive force due to electric charges. The discrepancy is often explained by assuming that the effective charge density of the poly-ion is much smaller than the analytical one due to ion binding or low activity coefficient of the counter-ion in the polymer domain. To explain the discrepancy may be the most important problem to be solved in this field, but before going into the problem it seems necessary to re-examine the theory of hydrodynamic resistance used for polyelectrolytes, considering the recent progress in the theory on excluded volume of nonionic polymers.

In most papers concerning the expansion of a polyion, the hydrodynamic resistance of the poly-ion is computed based on Flory's theory.² That is, the polymer coil is practically nondraining for solvent and the intrinsic viscosity is determined by the linear expansion of the polymer coil, α_η , as

$$[\eta] = KM^{1/2}\alpha_\eta^3 (= KM^\nu) \quad (1)$$

(1) S. A. Rice and M. Nagasawa, "Polyelectrolyte Solutions," Academic Press, Inc., New York, N. Y., 1961.

(2) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIV.

and

$$[\eta]_\theta = KM^{1/2} \quad (2)$$

That is

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \quad (3)$$

Here, $[\eta]_\theta$ is the intrinsic viscosity at θ temperature where the intrinsic viscosity is linear in the square root of molecular weight, $M^{1/2}$, as shown in eq. 2. The intrinsic viscosity $[\eta]$ is also related to the root-mean-square end-to-end distance $\langle h^2 \rangle^{1/2}$ by the equation³

$$[\eta] = \Phi \frac{\langle h^2 \rangle^{3/2}}{M} \quad (4)$$

where Φ is the well known universal constant of Flory.

To relate this expansion factor α_η with molecular constants of polymer and solvent, Flory derived the equation

$$\alpha_\eta^5 - \alpha_\eta^3 = CZ \quad (5)$$

where C is a numerical constant and Z is a function defined by

$$Z = \left(\frac{3}{2\pi a^2}\right)^{3/2} \beta \left(\frac{M}{m_s}\right)^{1/2} \quad (6)$$

In eq. 6, a is the length of a link; M and m_s , the molecular weights of polymer and segment, respectively; and β is the binary cluster integral defined by

$$\beta = -\int_0^\infty [1 - \exp(-V(r)/kT)] 4\pi r^2 dr \quad (7)$$

where $V(r)$ is the potential of average force between two segments as a function of their distance r . Although β is commonly used in this field, we prefer to use B converted from β by the relationship

$$B = \beta/2m_s^2 \quad (8)$$

for convenience of our discussion. Combination of eq. 5 and eq. 1 gives the following equation of Flory, Fox, and Schaeffgen³

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K^{2/3} + C'B \frac{M}{[\eta]} \quad (9)$$

(3) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

From the graphical plot of $[\eta]^{2/3}/M^{1/3}$ vs. $M/[\eta]$ one may evaluate both K and B , separately.

Flory's theory was criticized by many authors^{4,5} because of the Gaussian distribution he assumed for the distribution of segments. After many discussions about the problem, Kurata, Stockmayer, and Roig,⁶ Stockmayer and Fixman,⁷ as well as Ptitsyn⁸ succeeded in deriving very similar equations of closed form, that is

$$\alpha^3 - \alpha = \frac{4}{3}g(\alpha)Z \quad (10)$$

$$g(\alpha) = 3\alpha^3/(3\alpha^2 + 1)^{3/2}$$

$$\alpha^3 = 1 + 2Z \quad (11)$$

where α is the linear expansion factor of the mean radius of gyration and is related with α_η by⁴

$$\alpha_\eta^3 = \alpha^{2.43}$$

If eq. 10 or 11 is combined with eq. 1, taking into account the difference between α and α_η , we have

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.383\Phi_0Bg(\alpha_\eta)M^{2/3}/[\eta]^{1/3} \quad (12)$$

$$[\eta]/\sqrt{M} = K + 0.51\Phi_0B\sqrt{M} \quad (13)$$

where Φ_0 is the universal constant at θ point ($\sim 2.87 \times 10^{21}$). As in eq. 9 we can obtain K and B from the graphical plots of $[\eta]^{2/3}/M^{1/3}$ vs. $g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}$ or $[\eta]/\sqrt{M}$ vs. \sqrt{M} . Recently, Kurata and Stockmayer⁹ reanalyzed the data of many polymers published and showed very clearly that eq. 12 gives much better agreement with experimental results than eq. 9. That is, the plots of experimental data according to eq. 12 give the same intercept at $M^{2/3}/[\eta]^{1/3} = 0$ when various solvents are used for a polymer, whereas the plots according to eq. 9 do not give the same intercept at $M/[\eta] = 0$ for different solvents. In spite of the difference between models used in K. S. R. and S. F. theories, eq. 12 and 13 give almost identical results.⁷

Equations 12 and 13 are very convenient for studying the expansion of polyions too, since we can easily obtain the mutual excluded volume of segments β (or B) from viscosity data, and also it is possible to discuss B from the standpoint of electrostatic interaction between segments. There were some discussions published by Ptitsyn¹⁰ and Eisenberg and Woodside¹¹ along this line. Ptitsyn calculated B by assuming the Debye-Hückel ionic atmosphere around segments and inserted it into his equation, which is not shown here but analogous to eq. 10 and 11, for comparison with experimental results of carboxymethyl cellulose, poly-(phosphate), and poly-(acrylic acid). Great disagreement was observed, however, between calculated and experimental results. Eisenberg and Woodside calculated the excluded volume function Z of poly-(vinyl sulfonate) from the intrinsic viscosity data using eq.

(4) M. Kurata and H. Yamakawa, *J. Chem. Phys.*, **28**, 785 (1958); **29**, 311 (1958); and also M. Kurata, H. Yamakawa, and H. Utiyama, *Makromol. Chem.*, **34**, 139 (1959).

(5) M. Fixman, *J. Chem. Phys.*, **23**, 1656 (1955); **36**, 3123 (1962).

(6) M. Kurata, W. H. Stockmayer, and A. Roig, *ibid.*, **33**, 151 (1960); and also M. Kurata and W. H. Stockmayer, *Rept. Progr. Polymer Phys. Japan*, **5**, 23 (1962).

(7) W. H. Stockmayer and M. Fixman, *J. Polymer Sci. Part C*, **No. 1**, 137 (1963).

(8) O. B. Ptitsyn and Y. Y. Eisner, *J. Tech. Phys. U.S.S.R.*, **29**, 1117 (1959); and also O. B. Ptitsyn, *Vysokomolekul. Soedin.*, **1**, 1200 (1959); **3**, 1673 (1961).

(9) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolymeren Forsch.*, **3**, 196 (1963).

(10) O. B. Ptitsyn, *Vysokomolekul. Soedin.*, **3**, 1084, 1251 (1961).

(11) H. Eisenberg and D. Woodside, *J. Chem. Phys.*, **36**, 1844 (1962).

10 and showed that $Z/M^{1/2}$ is independent of molecular weight of polymer.

In this paper, eq. 9, 12, and 13 are compared by using the intrinsic viscosity data of sodium poly-(acrylate) of several different molecular weights in sodium bromide solutions of different concentrations. Much better agreement is observed in case of eq. 12 and 13 than in case of eq. 9. Moreover, from the slope of linear relationship of eq. 12 and 13 we evaluate B as a function of the concentration of sodium bromide and discuss it based on the electrostatic interaction theory of electrolytes.

Experimental

Polymer Samples.—Sodium poly-(acrylate) used in this investigation was kindly provided from Toa Gosei Chemical Co. and its viscosity average molecular weight was 160,000. The sample was purified by precipitation from aqueous solution with methanol three times and was used for fractionation.¹² One hundred grams of the purified sample was dissolved in 6 l. of 0.4 *N* NaOH aqueous solution and the fractional precipitation was carried out at 25° through repeated stepwise addition of methanol-water mixture of 1:1 volume ratio which also contained 0.4 *N* NaOH. Twelve fractions were obtained, but seven fractions having suitable molecular weights were used for measurements. Each fraction was purified by precipitation from aqueous solution by adding methanol twice and washed with 90% methanol until excess NaOH was removed. The samples thus purified were washed with absolute methanol and ether, and then dried at 50° in a vacuum oven for 2 weeks. When the samples were dissolved in pure water at about 0.1 *N*, the pH's of the solutions were 7~8.

Molecular Weight Determination.—Molecular weights of these fractions were determined from the intrinsic viscosities at 15° in 1.5 *N* NaBr solution (θ solvent¹³) using the equation

$$[\eta]_{1.5N NaBr} = 12.4 \times 10^{-4} M_w^{0.5} (15^\circ) \quad (14)$$

which was determined by using the light scattering method described previously.¹⁴ Molecular weights of each fraction thus determined are given in Table I.

TABLE I
MOLECULAR WEIGHTS OF SAMPLES USED FOR VISCOSITY MEASUREMENTS

$M \times 10^{-4}$	Fraction						
	FL4	FL3	F ₂ L7	F ₂ L6	F ₂ L4	F ₂ L1	FL1
	1.5	3.7	4.44	5.39	12.86	34.68	50.0

Preparation of Solutions.—Stock solutions of the fractionated samples and sodium bromide were prepared by weight using boiled distilled water; and the solutions having desired polymer and NaBr concentrations were made by mixing these stock solutions and boiled distilled water in volumetric flasks.

Viscosity Measurements.—Intrinsic viscosities of the fractionated samples in NaBr solutions of various concentrations were determined with a capillary viscometer of modified Ubbelohde type, which had three bulbs for giving rate of shear corrections to the measured viscosities. The volumes of the three bulbs were; top 1.49; middle, 1.50; lowest, 1.47 ml. The heights of the centers of the bulbs, measured with a cathetometer, were 8.73, 5.81, and 2.93 cm., respectively. The capillary maintained horizontally had the length of 20 cm. and the radius of 0.039 cm., determined from the weight of mercury contained in a given length. The average rate of shear on a given solution, γ , was calculated from the formula

$$\gamma = \frac{rhg}{3l\nu_0\eta_{rel}} = \frac{k}{\eta_{rel}}$$

with the assumption that the densities of solution and solvent are the same. Here r is the radius of capillary, h the pressure head, g the acceleration of gravity, l the length of capillary, ν_0 the kinematic viscosity of solvent and η_{rel} is the relative viscosity of solution to that of solvent. The factors k calibrated with the known kinematic viscosity of water at 15° were 469, 319, and 161 sec.⁻¹ for top, middle, and lowest bulbs, respectively.

A few examples of the rate of shear dependence of sample FL1 in NaBr solution are shown in Fig. 1. The examples selected are the measurements where the molecular weight is the highest, the ionic strength is almost the lowest, and the concentration is also the highest. Therefore, the rate of shear correction was

(12) A. Takahashi and I. Kagawa, *J. Chem. Soc. Japan, Ind. Chem. Section*, **64**, 1637 (1961) (in Japanese).

(13) A. Takahashi, S. Yamori, and I. Kagawa, *ibid.*, **83**, 11 (1962) (in Japanese).

(14) A. Takahashi, T. Kamei, and I. Kagawa, *ibid.*, **83**, 14 (1962) (in Japanese).

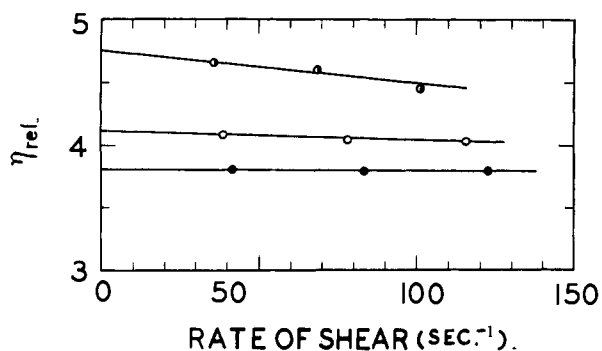


Fig. 1.—Relative viscosity as a function of rate of shear for sample FL1 at various ionic strengths of NaBr at 15°: ●, $C = 0.126$ g./100 ml., $C_s^\circ = 1 \times 10^{-2}$; ○, $C = 0.0945$ g./100 ml., $C_s^\circ = 5.02 \times 10^{-3}$; ◐, $C = 0.0945$ g./100 ml., $C_s^\circ = 2.51 \times 10^{-3}$.

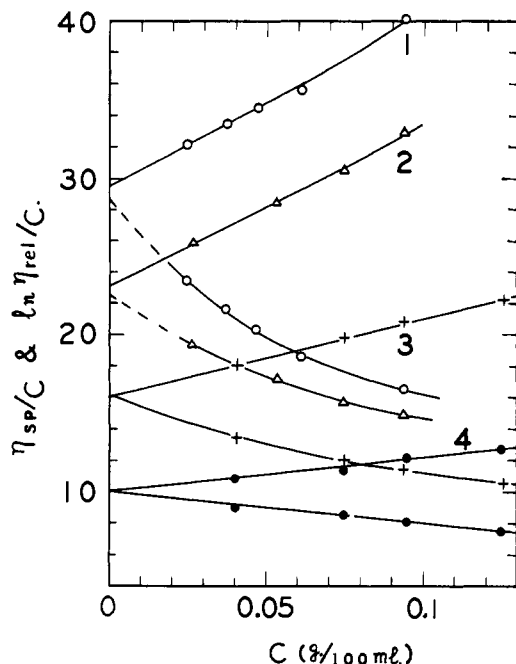


Fig. 2.—Selected viscosity-concentration plots for sample FL1 at various ionic strengths of NaBr at 15°: 1, $C_s^\circ = 2.51 \times 10^{-3}$; 2, $C_s^\circ = 5.02 \times 10^{-3}$; 3, $C_s^\circ = 1.00 \times 10^{-2}$; 4, $C_s^\circ = 2.51 \times 10^{-2}$.

unnecessary in most experiments other than such a few extreme cases (FL1 and F₂L1, NaBr concentration 0.0025 and 0.005 *N*).

The efflux times of water through these three bulbs at 15° were 52.7, 80.3, and 154.0 sec., respectively. The kinetic energy correction factors were estimated from the efflux times of water at 15 and 35°, and found to be 0.67, 0.27, and 0.8%, respectively. In most experiments where the rate of shear correction was unnecessary, only the middle bulb was used, and hence the kinetic energy correction could be neglected.

All measurements were carried out at $15.0 \pm 0.01^\circ$ for comparison with the data in θ solvent.^{13,14} All solutions were filtered through a sintered glass filter of JIS No. 4 prior to viscosity measurements. Dilutions were made by volume in the viscometer. The flow times were determined to 0.1 sec. A few examples in determining $[\eta]$ from η_{sp}/C vs. C and $\ln \eta_{rel}/C$ vs. C under the most severe conditions are shown in Fig. 2. In experiments 1 and 2 of Fig. 2, the rate of shear correction was applied, while in others the correction was negligible. The values obtained for the intrinsic viscosity were found to be reproducible within $\pm 5\%$ under such severe experimental conditions, but much better reproducibility was found under ordinary experimental conditions.

Results

Viscosity Equations at Various Ionic Strengths.—

All experimental results of intrinsic viscosities of the fractionated samples in NaBr solutions having different ionic strength are summarized in Table II. In Fig. 3 are shown the graphs of intrinsic viscosities vs. molecu-

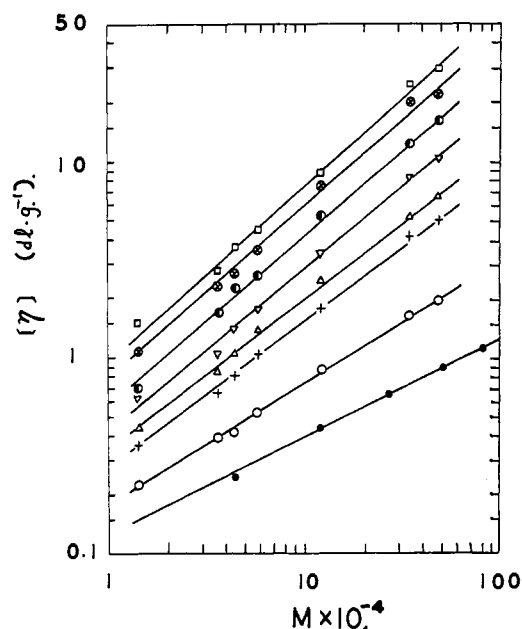


Fig. 3.—Intrinsic viscosity vs. molecular weights of sodium poly-(acrylate) in sodium bromide solutions at 15°; ionic strength of NaBr, C_s° : ●, 1.506; ○, 5.02×10^{-1} ; +, 1.00×10^{-1} ; Δ, 5.02×10^{-2} ; ▽, 2.51×10^{-2} ; ◐, 1.00×10^{-2} ; ⊗, 5.02×10^{-3} ; □, 2.51×10^{-3} .

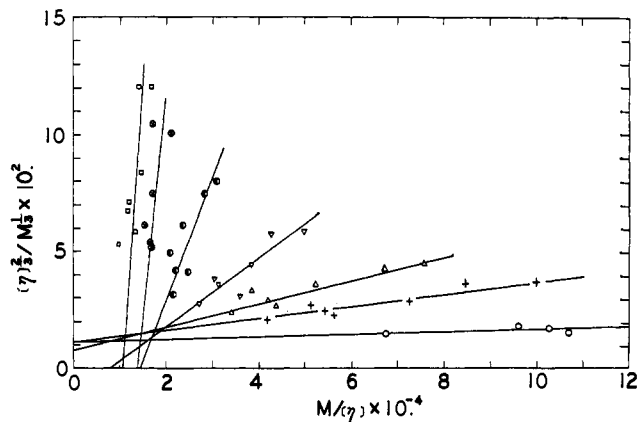


Fig. 4.—Flory, Fox, and Schaeffgen's plots (eq. 9); ionic strengths of NaBr are the same as in Fig. 3.

lar weights in logarithmic scale. The lowermost curve in Fig. 3, which are the data at the θ point, is reproduced from previous papers^{13,14} and the straight line has the theoretical slope of 0.5. As is clear from Fig. 3, the slope of $\log [\eta]$ vs. $\log M$ graphs increases with decreasing ionic strength and seems to reach as high as 0.9, as expected from K. S. R. and S. F. theories. The values of K as well as ν in the viscosity equation, $[\eta] = KM^\nu$, calculated from Fig. 3 by the least square method, are summarized in Table III. Considering the ambiguity in the experimental points at low ionic strength, however, we should avoid concluding the limiting value of ν at low ionic strength.

Comparison between Experimental Data and Theoretical Equations.—In Fig. 4, Flory, Fox, and Schaeffgen's equation is compared with experimental results, and Kurata, Stockmayer, and Roig's plots and Stockmayer and Fixman's plots are shown in Fig. 5 and 6, respectively. Despite the prediction of these theories that all straight lines in each figure should give the same intercept, actually it is observed that straight lines in Fig. 5 or 6 give almost the same intercept—at least to the extent that straight lines drawn from the same

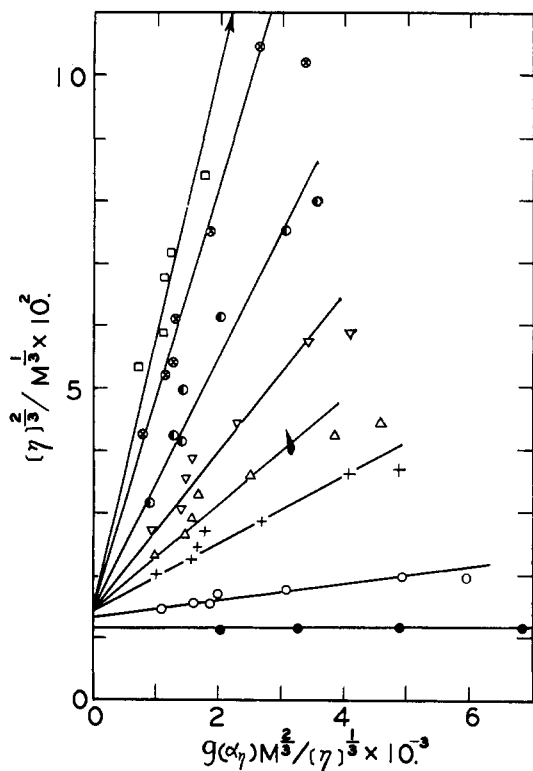


Fig. 5.—Kurata, Stockmayer, and Roig's plots (eq. 12); ionic strengths of NaBr are the same as in Fig. 3.

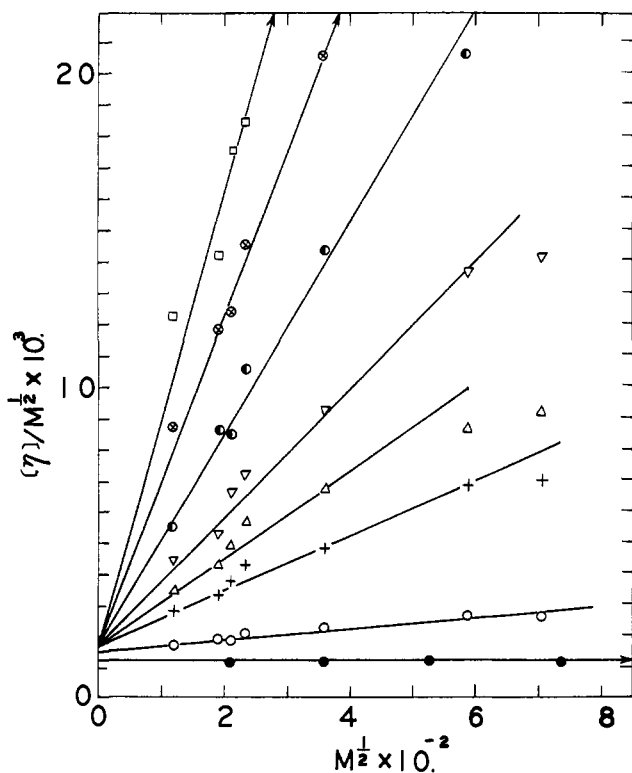


Fig. 6.—Stockmayer and Fixman's plots (eq. 13); ionic strengths of NaBr are the same as in Fig. 3.

point do not look unreasonable—but the plots of Flory, *et al.*, in Fig. 4 do not seem to converge at the same point even though the ambiguity in experimental points is taken into account. This situation is the same as that observed for nonionic polymers, which was fully discussed by Kurata and Stockmayer.⁹ Therefore, we may determine the value of K from the intercept and B

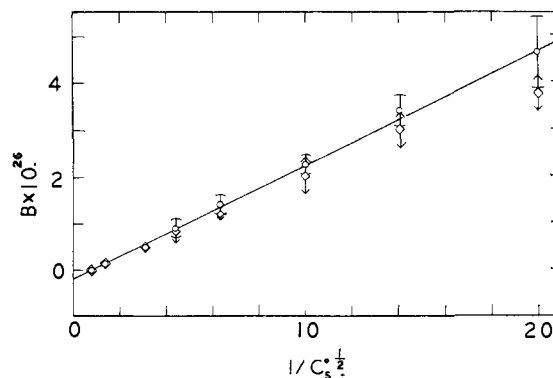


Fig. 7.— B vs. inverse root of ionic strength $1/C_s^{1/2}$: O, B obtained from S. F. plots; \diamond , B obtained from K. S. R. plots.

from the slope of the straight lines in Fig. 5 and 6. The values of B determined from both theories are shown in Fig. 7 for comparison. Since the experimental points in Fig. 5 and 6 scatter considerably at low ionic strength, it is true that the values of B obtained have considerable ambiguity at low ionic strength, but at high ionic strength the values are very reliable. The ambiguity in B thus obtained is indicated in Fig. 7.

TABLE II
INTRINSIC VISCOSITIES OF SODIUM POLY-(ACRYLATE) IN AQUEOUS SOLUTIONS OF SODIUM BROMIDE AT 15°

C_s° , moles/l.	Fraction						
	FL4	FL3	F ₂ L7	F ₂ L6	F ₂ L4	F ₂ L1	FL1
1.506	0.149	0.238	0.260	0.300	0.437	0.735	0.883
5.02×10^{-1}	.222	.385	.414	0.525	0.860	1.645	1.917
1.00×10^{-1}	.358	.655	.817	1.048	1.77	4.09	5.00
5.02×10^{-2}	.438	.841	1.05	1.396	2.45	5.15	6.58
2.51×10^{-2}	.550	1.029	1.41	1.76	3.34	8.13	10.05
1.00×10^{-2}	.689	1.68	1.78	2.58	5.20	12.2	16.0
5.02×10^{-3}	1.08	2.29	2.64	3.52	7.42	19.95	23.17
2.51×10^{-3}	1.51	2.74	3.72	4.45	8.72	24.7	29.6

TABLE III
DEPENDENCE OF K AND ν IN VISCOSITY EQUATION ($[\eta] = KM^\nu$) ON IONIC STRENGTH AT 15°

C_s° , moles/l.	$K \times 10^4$	ν
1.504 ¹⁴	12.4	0.5
5.02×10^{-1}	5.27	.628
1.00×10^{-1}	2.54	.755
5.02×10^{-2}	2.81	.77
2.51×10^{-2}	1.63	.84
1.00×10^{-2}	(1.36)	.89
5.02×10^{-3}	(4.42)	.83
2.51×10^{-3}	(2.49)	.89

Here, it is to be noted that B obtained is proportional to the inverse root of ionic strength of solvents, $1/\sqrt{C_s^\circ}$, at least when the ionic strength is not too low, while Flory and Osterheld¹⁵ showed by using Flory's theory¹⁶ that B is proportional to the inverse of ionic strength, $1/C_s^\circ$. In our experiments, too, B would be proportional to the inverse of ionic strength if we evaluate B from Flory's theory at a constant molecular weight. Besides, it is interesting to see that B at infinite ionic strength is negative.

The values of K obtained from Fig. 5 and 6 are almost equal and, hence, only the values determined from Fig. 6 are listed in Table IV. Strictly speaking, it is observed that K depends slightly on the ionic strength of solvent. The unperturbed dimensions of polymers, $\langle h_0^2 \rangle^{1/2}$, can be calculated from K using the relationship

(15) P. J. Flory and J. E. Osterheld, *J. Phys. Chem.*, **58**, 653 (1954).

(16) P. J. Flory, *J. Chem. Phys.*, **21**, 162 (1953).

$$K = \Phi_0 \left(\frac{\langle h_0^2 \rangle}{M} \right)^{3/2}$$

The ratios of $\langle h_0^2 \rangle^{1/2}$ to $\langle h_{0f}^2 \rangle^{1/2}$, the unperturbed dimension for the case of free rotation around individual chain bond, are also listed in Table IV and are found to be almost equal to those reported for nonionic polymers.⁹

Intrinsic Viscosity of Polyelectrolyte as a Function of Molecular Weight and Ionic Strength.—The inspection of Fig. 7 shows that B determined experimentally is expressed as

$$B = B_0 + B_e = B_0 + (A/\sqrt{C_s^\circ}) \quad (15)$$

where A is a numerical constant, B_0 the value of B at infinite ionic strength (that is, the term due to nonelectrostatic interaction), and B_e is the term due to the electrostatic interaction. By inserting this equation into eq. 13, we obtain

$$[\eta]/\sqrt{M} = K + 0.51\Phi_0(B_0 + A/\sqrt{C_s^\circ})\sqrt{M} \quad (16)$$

At constant molecular weight, this reduces to

$$[\eta] = (\text{const.})_1 + (\text{const.})_2 \frac{1}{\sqrt{C_s^\circ}} \quad (17)$$

This is the equation presented first by Pals and Hermans¹⁷ and later confirmed for many polyelectrolytes by Cox.¹⁸

TABLE IV

UNPERTURBED END-TO-END DISTANCES AT VARIOUS IONIC STRENGTHS

C_s° , moles/l.	$K \times 10^3$	$\{ \langle h_0^2 \rangle / M \}^{1/2} \times 10^{11}$	$\{ \langle h_0^2 \rangle / \langle h_{0f}^2 \rangle \}^{1/2}$
1.506	1.24	756	2.38
5.02×10^{-1}	1.5	805	2.5
1.00×10^{-1}	1.6	822	2.6
5.02×10^{-2}			
$\sim 5.02 \times 10^{-3}$	1.6	822	2.6

When $B_0 = -B_e$, we have $B = 0$, that is, the θ point of the polyelectrolyte in salt solution. At this point, the osmotic second virial coefficient also becomes zero.¹⁸ Therefore, it can be concluded that aqueous salt solution is a very poor solvent for the discharged poly-ion.

Discussion

The assumptions involved in the excluded volume theory of nonionic polymers are: (1) The free energy of one macromolecule in solvent is the sum of the configurational entropy of polymer skeleton and the interaction energies of all possible pairs of segments. (2) The potential of average force, $V(r)$, rapidly drops off with distance between segments, and the mutual excluded volume β is significantly smaller than the volume occupied by a polymer coil, *i.e.*, $\beta \ll \langle h^2 \rangle^{3/2}$. (3) There is no requisite for the functional form of this potential.

The extension of the excluded volume theory of nonionic polymers to polyelectrolytes was first carried out by Ptitsyn.¹⁰ To calculate β , he assumed that the potential of average force is the sum of two terms, nonionic ($V_0(r)$) and ionic ($W(r)$).

$$V(r) = V_0(r) + W(r) \quad (18)$$

and

$$V_0(r) \gg W(r) \text{ for } r \leq a_0 \\ V_0(r) = 0 \text{ for } r > a_0$$

if we denote the distance of the closest approach of segments by a_0 . As was done by Hill,¹⁹ $W(r)$ is assumed to be given by the Debye-Hückel theory; that is

(17) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 456 (1952).

(18) R. A. Cox, *J. Polymer Sci.*, **47**, 441 (1960).

(19) T. L. Hill, *Discussions Faraday Soc.*, **21**, 31 (1956); *J. Phys. Chem.*, **61**, 458 (1957); and also D. Stigter and T. L. Hill, *ibid.*, **63**, 551 (1959).

$$W(r) = \frac{Z_s^2 e^2}{D} \frac{e^{\kappa a_0}}{1 + \kappa a_0} \frac{e^{-\kappa r}}{r} \quad (19)$$

with

$$\kappa^2 = \frac{8\pi e^2 N_A}{DkT} \times 10^3 C_s^\circ$$

where Z_s is the charge number of a segment, D the dielectric constant of solvent, e the unit charge, N_A the Avogadro number, and C_s° is the concentration of added neutral salt of 1:1 type expressed in mole/l. If the concentration of added salt is so high that $W(r)/kT \ll 1$ may be assumed, the mutual excluded volume β or B can be approximated in the form

$$B = B_0 + B_e \quad (20)$$

$$B_e = \frac{10^3}{4m^2 N_A C_s^\circ}$$

with

$$m = m_s/Z_s$$

If we use Flory's theory² on the excluded volume of nonionic polymers for B_0 , we can express it as

$$B_0 = \frac{V_1}{N_A} \left(\frac{1}{2} - \chi_1 \right) \frac{1}{m_s^2} \quad (21)$$

where χ_1 is Flory's interaction parameter and V_1 the molar volume of solvent. This form of B is the form derived also by Eisenberg and Woodside.¹¹

Since B_0 is not much influenced by change in the concentration of added salt, it is expected from eq. 20 that B should be proportional to $1/C_s^\circ$. However, our experimental results as shown in Fig. 7 clearly show that B is proportional to $1/\sqrt{C_s^\circ}$. In addition to this discrepancy in the functional form, there is great disagreement between the absolute values of B determined by experiment and calculated from eq. 20. The calculated values are from 50 to 400 times larger than the experimental ones (see Table V). One might suppose

TABLE V

COMPARISON BETWEEN VALUES OF B_e DETERMINED FROM S. F. PLOTS AND CALCULATED FROM EQ. 20;

$$B_{\text{obsd}} = -0.2 \times 10^{-26} + B_e$$

C_s° , moles/l.	$B_e \times 10^{26}$ (obsd.)	$B_e \times 10^{26}$ (calcd.)
1.506	0.2	3.13
5.02×10^{-1}	$.32 \pm 0.01$	9.4
1.00×10^{-1}	$.7 \pm .05$	47
5.02×10^{-2}	$1.1 \pm .2$	94
2.51×10^{-2}	$1.6 \pm .2$	188
1.00×10^{-2}	$2.46 \pm .2$	470
5.02×10^{-3}	$3.6 \pm .3$	940
2.51×10^{-3}	$4.8 \pm .8$	1880

that the reason for this discrepancy is the use of the Debye-Hückel approximation in calculating the interaction energy between two segments, eq. 19, because it is often said that the ionic atmosphere around fixed charges of the poly-ion is much different from one of the Debye-Hückel type. However, the failure of the Debye-Hückel approximation for polyelectrolytes cannot be the main reason for this discrepancy. The electrostatic potential around rod-like poly-ion calculated from the Poisson-Boltzmann equation with the assumption of the Debye-Hückel approximation was compared with the potential obtained without this assumption.^{20,21} The difference between both calculated results was fairly large at low ionic strength, but was not as great at high ionic strength. Judging from the results obtained for the rod-like poly-ion, it is clear that the failure of the Debye-Hückel approximation is not the main reason for the extremely low experimental

(20) L. Kotin and M. Nagasawa, *J. Chem. Phys.*, **36**, 873 (1962).

(21) Z. Alexandrowicz, *J. Polymer Sci.*, **56**, 97 (1962).

values of B for our present model, particularly when the ionic strength is high.

According to our opinion, the reason for the discrepancy is that the free energy of coiled polymer expressed by the sum of the pairwise interactions between segments ($1/2\beta\int\rho^2(r)dr$) is not adequate for a poly-ion. That is, following the discussion of Kurata, Stockmayer, and Roig⁶ or Hermans and Overbeek,²² the average square end-to-end distance of a poly-ion is given by

$$\langle h^2 \rangle = \frac{\int h^4 \exp\left(-\frac{3h^2}{2Na^2} - \frac{F_0}{kT} - \frac{F_{el}}{kT}\right) dh}{\int h^2 \exp\left(-\frac{3h^2}{2Na^2} - \frac{F_0}{kT} - \frac{F_{el}}{kT}\right) dh} \quad (22)$$

where F_0 and F_{el} are the nonelectrostatic and electrostatic parts of the free energy of one polymer system, respectively, corresponding to B_0 and B_e of eq. 20. The calculation of this equation can be carried out by taking the maximum term of the following function, as usual

$$\alpha^3 \exp\left(-\frac{3}{2}\alpha^2 - \frac{F_0}{kT} - \frac{F_{el}}{kT}\right)$$

where the symbol α is

$$\alpha^2 = h^2/Na^2$$

Thus, we have

$$\alpha^3 - \alpha = -\frac{\alpha^2}{3} \frac{\partial(F_0/kT)}{\partial\alpha} - \frac{\alpha^2}{3} \frac{\partial(F_{el}/kT)}{\partial\alpha} \quad (23)$$

For nondraining coil, combination of eq. 1, 2, and 23 leads to

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K^{2/3} - \frac{1}{3} K^{2/3} \left[\alpha \frac{\partial(F_0/kT)}{\partial\alpha} + \alpha \frac{\partial(F_{el}/kT)}{\partial\alpha} \right] \quad (24)$$

If we employ the calculation of Kurata, *et al.*,⁶ on an ellipsoidal model for F_0 , eq. 24 can be transformed into

$$\frac{[\eta]^{2/3}}{M^{1/3}} = K^{2/3} + C_1 g(\alpha) \left[B_0 + \frac{C_2}{g(\alpha)M^{1/2}} \alpha^2 \frac{\partial(F_{el}/kT)}{\partial\alpha} \right] \frac{M^{2/3}}{[\eta]^{1/3}} \quad (25)$$

Thus

$$B_e = \frac{C_2}{g(\alpha)M^{1/2}} \alpha^2 \frac{\partial(F_{el}/kT)}{\partial\alpha} \quad (26)$$

The derivation of this equation has been based on the ellipsoidal model of Kurata, *et al.* However, considering the facts that both K. S. R. and S. F. theories give almost the same results and also that $g(\alpha)$ term which comes from the ellipsoidal model does not change by more than 40% over our experimental range, we can safely presume that the viscosity equation of polyelectrolytes has the following form, in general

$$\frac{[\eta]}{\sqrt{M}} = K + C_4 \left[B_0 + C_3 \frac{1}{\sqrt{M}} \alpha^2 \frac{\partial(F_{el}/kT)}{\partial\alpha} \right] \sqrt{M} \quad (27)$$

or

$$B_e = C_3 \frac{1}{\sqrt{M}} \alpha^2 \frac{\partial(F_{el}/kT)}{\partial\alpha} \quad (28)$$

Only if F_{el} could be expressed by the sum of pairwise interaction between segments would the B_e term become eq. 20 or its analogous form. However, the electrostatic free energy of electrolyte solutions cannot be expressed in such a simple way but should contain all interactions among ions. Therefore, it is our opinion

(22) J. J. Hermans and J. Th. G. Overbeek, *Rec. trav. chim.*, **67**, 761 (1948).

that the neglect of counterion-counterion interaction and counterion-segment interaction may be the main reason for the disagreement between eq. 20 and our experimental results.²³

Now, by comparing eq. 28 with our experimental results, eq. 15, we can presume the functional form which F_{el} should take to explain the viscosity behavior of polyelectrolytes. That is

$$F_{el} \propto \frac{1}{\sqrt{C_s^0}} \frac{\sqrt{M}}{\alpha} \quad (29)$$

There are many theories published for calculating the electrostatic free energy of a poly-ion, but there is no satisfactory theory from this point of view. Strictly speaking, however, the exponent of C_s^0 may be between 0.5 and 0.6 as Cox also mentioned in his paper,¹⁸ and the reliability of the form \sqrt{M}/α depends on the reliability of the functional form of S. F. theory.

One of the features of the study on polyelectrolyte viscosity is that it is possible to change the radius of gyration without changing the molecular weight of polymer. Hence, the expansion of poly-ion accompanies the vigorous change of the segment density inside the poly-ion domain, whereas the segment density inside most nonionic polymers is not changed so vigorously in the ordinary experimental range. From the present experiments, it is likely that the change in the segment density inside the polymer domain does not give any essentially important effect on the viscosity, but the viscosity is mainly determined by the radius of gyration. However, considering the fact that the viscosity of star molecules recently studied^{24,25} may depend on the segment density inside the polymer domain and also that the segment density inside polyion domain is extremely low at low ionic strength, we need more experimental facts to reach a final conclusion on the effect of the segment density on the intrinsic viscosity and on whether the highly expanded poly-ion at low ionic strength is really nondraining.

Finally, unperturbed dimension of nonionic polymer is determined by short range interaction of polymer constituents. It is usually independent of solvents, if measurements are made at the same temperature. In case of polyelectrolytes, however, there is a possibility¹¹ that a part of the short range interaction may be of the electrostatic nature and, therefore, the unperturbed dimension may be influenced by ionic strength at the same temperature. Our data show that there may be such an effect but it is small. That is, it is observed that the intercepts of K. S. R. and S. F. plots in Fig. 5 and 6 (which both give K) slightly depend on the ionic strength of solution.

Acknowledgments.—We wish to express our thanks to Professor Michio Kurata of Kyoto University who gave us his valuable suggestions throughout this research, to Professor Ikumi Kagawa of Nagoya University for his encouragement, and also to Drs. K. Ōhashi and S. Suzuki of Toa Gosei Chemical Co. for supplying us the sample of sodium poly-(acrylate). We are also indebted to Mr. M. Ōta for his assistance in measuring viscosities and to Mr. M. Tasaka for his translation of Russian literature.

(23) M. Nagasawa, *J. Am. Chem. Soc.*, **83**, 300 (1961).

(24) B. H. Zimm and R. W. Kilb, *J. Polymer Sci.*, **37**, 19 (1959).

(25) T. A. Orofino and F. Wenger, *J. Phys. Chem.*, **67**, 566 (1963).