The conditions under which analysis of spectra is possible to quantitatively determine intramolecular motion are fairly restricted. The molecular weight must be such that at the lowest angles of measurement x is small (less than about 0.5, judging from Figure 8), so that only the translational motion contributes to the spectrum and a value of D may be obtained. At the highest scattering angles x must be about 2–3 so that the maximum possible contribution from the dominant intramolecular term will be observed while contributions from other intramolecular motions remain negligible.

Finally, the fact that even a small amount of polydispersity is predicted to cause some excess broadening and some spectral distortion at high values of x because of its influence on the spectrum due to translation alone implies that samples having very narrow molecular weight distributions must be used if effects of polydispersity are not to interfere with quantitative determination of intramolecular motion.

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Solution Properties of Novel Polyelectrolytes[1]

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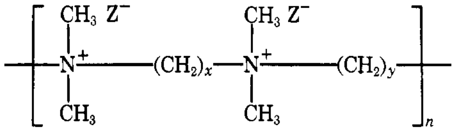
ABSTRACT: A series of polyelectrolytes, of different molecular weights, with the unit segment structure



$$\left[-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_x-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_y- \right]_n$$

were synthesized through the Menschutkin reaction and are referred to as ionene polymers. The solution properties of a high charge density ionene polymer (3,4 Br, $x = 3$, $y = 4$, Z = Br) were compared with those of an ionene polymer in which the positive charges are separated by six CH_2 groups (6,6 Br, $x = 6$, $y = 6$, Z = Br). These polyelectrolytes, when dissolved in aqueous 0.4 M KBr, were found to approximate the behavior of conventional polymers. The intrinsic viscosity–molecular weight relationship in aqueous 0.4 M KBr was determined for 3,4 Br and 6,6 Br by means of the light-scattering technique and can be expressed by $[\eta]_{3,4Br} = (2.94 \times 10^{-4})M^{0.61}$ and $[\eta]_{6,6Br} = (6.22 \times 10^{-4})M^{0.58}$. A viscosity study as a function of concentration of a number of potassium salts in water revealed that the reduced viscosity of a 6,6 Br increases as the anions change in the following order: $CNS^- < I^- < NO_3^- < Br^- < Cl^- < F^-$. This trend is attributed to a parallel decrease of counterion site binding. In the absence of added salts, the viscosity behavior is adequately represented by the Fuoss equation.

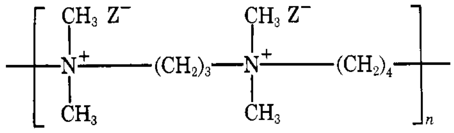
The solution properties of polyelectrolytes are currently of considerable interest. Although a substantial amount of work has been carried out using polyanions, only a limited number of investigations have been performed to elucidate the properties of polycations.

One class of polycations, quaternary ammonium polymers which are readily prepared by means of the Menschutkin reaction,[2] has so far received very little attention. The structure of these cationic polyelectrolytes, termed ionenes, has recently been established,[3] and for several reasons ionenes are ideally suited for a study of polycation behavior. First, their synthesis is simple and straightforward; second, the chains are not branched; third, their molecular weights are in a low range where the viscosity behavior is not complicated by a velocity gradient dependence; and fourth, the charge density in the polymer backbone can be varied readily.

This paper describes part of a study into the solution properties of ionene polymers, covering light-scattering and viscosity measurements.

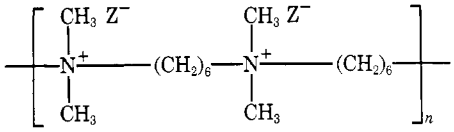
Experimental Section

The 3,4 and 6,6 ionene polymers, having the unit segment structures I and II, respectively, where Z = Br or Cl and n = degree of



$$\left[-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_3-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_4- \right]_n$$

I (3,4 Z)



$$\left[-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_6-\overset{CH_3\ Z^-}{\underset{CH_3}{N^+}}-(CH_2)_6- \right]_n$$

II (6,6 Z)

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[1] This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100, sponsored by the National Aeronautics and Space Administration.

[2] A. Rembaum, *J. Macromol. Sci., Chem.*, **3**, 87 (1969); W. Kern and E. Brenneisen, *J. Prakt. Chem.*, **159**, 193 (1941); C. F. Gibbs and C. S. Marvel, *J. Amer. Chem. Soc.*, **57**, 1137 (1935).

[3] N. Noguchi and A. Rembaum, *J. Polym. Sci., Part B*, **7**, 383 (1969).

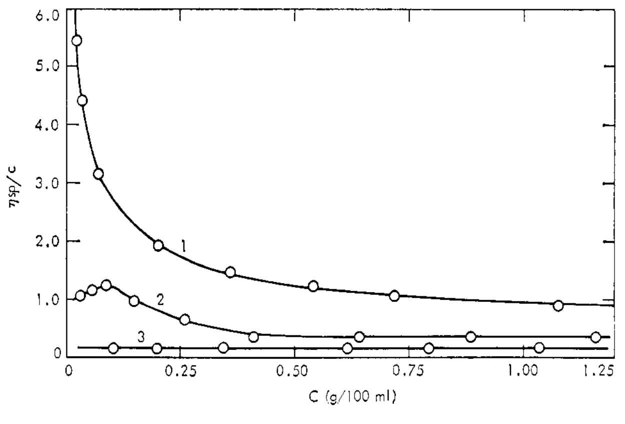

Figure 1. Reduced viscosity of 6,6 Br solution as a function of polyelectrolyte concentration, *C*. Solvents: H_2O, 1; 0.05 *M* KBr, 2; 0.40 *M* KBr, 3.

TABLE I
VISCOSITY DATA FOR IONENES IN 0.4 *M* SALT SOLUTION

Ionene	Salt	$[\eta]$, dl/g	*k* (eq 1)
3,4 Br[a]	KBr	0.162	0.361
		0.176	0.335
		0.231	0.344
		0.250	0.333
		0.304	0.339
6,6 Br[b]	KBr	0.155	0.369
		0.192	0.376
		0.210	0.388
		0.319	0.370
		0.331	0.365
6,6 Cl[b]	KBr	0.116	0.360
		0.150	0.384
		0.177	0.361
		0.218	0.372
6,6 Cl[b]	KCl	0.145	0.283
		0.179	0.279
		0.242	0.290
		0.290	0.293

[a] Prepared in dimethylformamide–methanol mixtures as described in ref 5 and precipitated from solution with acetone to yield fractions differing in $[\eta]$. [b] Prepared from *N,N,N′,N′*-tetramethyl-1,6-hexanediamine and either 1,6-dibromohexane or 1,6-dichlorohexane. Experimental procedure was described in ref 4.

polymerization, were prepared as described previously.[2,3] Samples over a range of molecular weights were obtained by varying reaction conditions, *i.e.*, temperature, solvent and concentration.

It was not considered necessary to fractionate these polyelectrolytes, since, for a step-growth polymerization,[4] the ratio of the weight-average to number-average molecular weights does not exceed 2.

Viscosities of all polymer samples were determined at 25.0° (±0.01°), using the same Cannon-Ubbelohde viscometer. No correction for shear dependency was applied, since only low molecular weight polymers were investigated. A Hewlett-Packard auto viscometer (Model 5901B) and a Hewlett-Packard programmer (Model 5901A) were used to measure and record the viscosity data.

Light-scattering measurements were made on solutions of the polymers, in the presence of added salts, using square 3-cm cells in a Brice-Phoenix light-scattering photometer. Measurements were made with unpolarized light at both the blue (4358 Å) and the green (5461 Å) mercury lines. The instrument was calibrated with a standard opal glass[5] and the calibration checked by determining Rayleigh's ratios at 90°, for unpolarized incident light, using both benzene and methanol. The values obtained were in good agreement with accepted values for these solvents. To remove dust, each polymer solution was pressure filtered through an ultrafine sintered-glass filter, at approximately 3.5×10^4 N/m^2 of pure nitrogen, directly into a clean light-scattering cell. Only solutions which appeared perfectly clear when visually observed at a low angle in a strong beam of light were accepted for light-scattering measurements.

To determine turbidities, scattering ratios at the 90° angle were measured, by the usual procedure, at several polymer concentrations. No corrections to the measured turbidities were required, since depolarization, light absorption, and fluorescence effects were found to be negligible. Refractive index differences between solutions and solvents were measured in a Brice-Phoenix differential refractometer, which had previously been calibrated by means of sucrose solutions. All turbidity and refractive index data were obtained at 20° (±1°).

Results and Discussion

(A) Viscosity. The viscosity, η, of dilute solutions of uncharged polymers can usually be represented, over a reasonably large range of concentrations, as a linear function of concentration

$$(\eta - \eta_0)/\eta_0 c = \eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (1)$$

where η_0 is the viscosity of the solvent, $[\eta]$ is the intrinsic viscosity, c is the concentration in grams of solute per 100 ml of solution, and k is a dimensionless constant (Huggins constant) characteristic of the polymer and solvent but usually independent of the molecular weight. The viscometric behavior of solutions of pure polyelectrolytes is, however, radically different from that of polyelectrolyte solutions with added salts. Fuoss[6] reported that the reduced viscosity, η_{sp}/c, of solutions containing a pure, highly charged, flexible, linear polyelectrolyte increased sharply and continuously with dilution at very low concentration. The observed concentration dependence of η_{sp}/c could be represented by the empirical relationship

$$\eta_{sp}/c = \frac{A}{1 + B\sqrt{c}} + D \qquad (2)$$

where *A*, *B*, and *D* are constants characteristic of each sample.

When a simple salt is added to a polyelectrolyte solution, some of the mobile electrolyte diffuses into the polyion coils. The resulting electrostatic screening of the charged segments by the electrolyte causes a marked reduction in the repulsive potential between segments, and the polyions contract, with a corresponding decrease in the viscosity of the solution. The reduced viscosity of a polyelectrolyte solution which contains excess of simple salt generally increases in a linear manner with increasing polymer concentration, in accordance with eq 1. This behavior has previously been observed for ionenes[4] and has now been investigated more thoroughly.

The effect of added electrolyte on the plots of reduced viscosity *vs.* ionene concentration is typical of that observed for many other polyelectrolytes.[7] A representative set of results is shown in Figure 1.

In 0.4 *M* salt solution, the viscosity of ionene polyelec-

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(4) A. Rembaum, H. Rile, and R. Somoano, *J. Polym. Sci., Part B*, **8**, 457 (1970).

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trolytes can be accurately represented by eq 1. The results of the viscosity studies in 0.4 M salt solution are given in Table I. Theoretically the slopes of the η_{sp}/c *vs.* c plots do not correspond to the true Huggins constants of eq 1, since dilution was carried out simply by addition of solvent and not by a dialysis technique which enables the chemical potential of all diffusible components to be kept constant. However, in 0.4 M salt solution and low polymer concentrations, the change in chemical potential on dilution is negligible. The most concentrated solution of 3,4 Br was only 0.05 M with respect to the counterion, and, for reasons to be discussed later, the actual concentration of "free" bromide ions, due to the polyelectrolyte, is thought to be much less than calculated above.

The results in Table I indicate that k (eq 1) is independent of molecular weight and has a value comparable to that obtained for uncharged polymer molecules.[8] It is noticeable that k for the 6,6 Cl in 0.4 M KCl is lower than k for any of the other systems. It is known that k values can be correlated with solute–solvent interaction. Increase in the value of k indicates a poorer solvent and approach to the Θ conditions. The lower value of k in the latter solvent is therefore consistent with results obtained by Strauss,[9] who has shown that for the sodium polyphospate–sodium bromide system, k increases with sodium bromide concentration as the latter approaches the composition of a Θ solvent. Similar behavior of k has been reported for nonionic polymer systems.[10,11] The data obtained from light-scattering measurements confirm the conclusions concerning the low value of k for the KCl solvent system (see section B).

In the complete absence of added electrolyte, the viscosity of the 3,4 Br and 6,6 Br ionenes was typical of polyelectrolytes and could be very accurately represented by eq 2. The results were fitted to this relationship by plotting $(\eta_{sp}/c - D)^{-1}$ *vs.* $c^{1/2}$. D was first approximately obtained for a plot of η_{sp}/c *vs.* $c^{-1/2}$,[12] and the values of D so obtained were found to produce perfectly linear plots of $(\eta_{sp}/c - D)^{-1}$ *vs.* $c^{1/2}$. The results are shown in Table II.

From eq 2, the value of η_{sp}/c as c approaches zero is equal to $A + D$, and since $D \ll A$, then A is the value of the intrinsic viscosity of pure polyelectrolyte in water. The intercept of the plot of $(\eta_{sp}/c - D)^{-1}$ *vs.* $c^{1/2}$ is equal to $1/A$, and the slope is equal to B/A. It was not possible to determine the values of A very precisely, because of their small magnitudes, and the error in A could amount to 20%. However, a plot of log A *vs.* log $\bar{M}_v$ for both systems produces a reasonably straight line with slopes of approximately 2.0, a value close to that theoretically predicted for stiff rodlike molecules,[13] which has also been observed experimentally.[14,15]

The relationships between A and molecular weight are given by the expressions

$$\text{3,4 Br} \qquad A = (3.1 \times 10^{-7})M^{2.0} \tag{3}$$

$$\text{6,6 Br} \qquad A = (2.3 \times 10^{-7})M^{2.0} \tag{4}$$

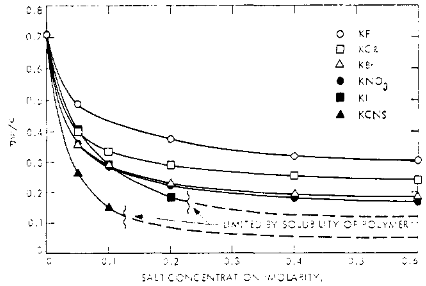

Figure 2. Reduced viscosity of 6,6 Br as a function of added salt concentration. Polyelectrolyte concentration 1.0 g/100 ml.

TABLE II

FUOSS EQUATION PARAMETERS

Ionene	$\bar{M}_v{}^a \times 10^{-4}$	D	$1/A$	B/A	A	B
3,4 Br	0.72	0.060	0.050	7.50	20.0	100
	1.28	0.045	0.020	3.70	50.0	185
	2.03	0.075	0.010	2.14	100.6	214
	2.77	0.020	0.003	1.08	330.0	356
	5.18	0	0	0.57	∞	
	6.38	0	0	0.36	∞	
6,6 Br	0.55	0.095	0.150	6.48	6.7	43.2
	0.94	0.105	0.050	3.84	20.0	76.7
	1.32	0.115	0.025	2.28	40.0	91.2
	1.64	0.110	0.010	1.21	100.0	120.8
	2.36	0.100	0.010	1.22	100.0	122.4
	2.63	0.100	0.005	0.98	200.0	197.0

[a] From smoothed plots of log $[\eta]$ *vs.* log M.

The parameter B of eq 2 also increases with increasing molecular weight. Using the data of Table II, a plot of log A/B *vs.* log $\bar{M}_v$ for the ionenes produces the following relationships

$$\text{3,4 Br} \qquad A/B = (4.0 \times 10^{-7})M^{1.42} \tag{5}$$

$$\text{6,6 Br} \qquad A/B = (6.0 \times 10^{-6})M^{1.18} \tag{6}$$

Combination of eq 3 and 5 and 4 and 6 leads to the expressions

$$\text{3,4 Br} \qquad B = (0.77)M^{0.82} \tag{7}$$

$$\text{6,6 Br} \qquad B = (0.04)M^{0.58} \tag{8}$$

The dependence of B on molecular weight is shown to be comparable to that observed by Strauss[15] for polyphosphates. In contrast to the polyphosphates, however, the parameter D of eq 2 does not appear to be dependent upon molecular weight and does not show any correlation with intrinsic viscosity measured in 0.4 M KBr solution.

The dependence of the reduced viscosity on the nature of the added electrolyte was examined for a 6,6 Br sample, and the results are shown graphically in Figure 2. The concentration of polymer was held constant at 1.0 g/100 ml, while the salt concentration was varied from zero to 0.6 M. It is readily apparent from Figure 2 that the reduced viscosity is almost constant above a salt concentration of approximately 0.3 M. The results obtained so far, together with light-scattering information to be discussed in the next section, indicate that in 0.4 M KBr solution the 6,6 Br behaves essentially like a neutral polymer. The increased value of η_{sp}/c in 0.4 M KCl or KF could be due either to a decrease in the number of "bound" counterions and hence expansion of the polymer coil or to intermolecular association between

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[9] U. P. Strauss, *J. Polym. Sci.*, **33,** 291 (1958).
[10] T. Alfrey, Jr., A. I. Goldberg, and J. A. Price, *J. Colloid Sci.*, **5,** 251 (1950).
[11] L. H. Cragg and R. H. Sones, *J. Polym. Sci.*, **9,** 585 (1952).
[12] W. N. Maclay and R. M. Fuoss, *ibid.*, **6,** 511 (1951).
[13] J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19,** 281 (1951).
[14] U. P. Strauss, E. H. Smith, and P. L. Wineman, *J. Amer. Chem. Soc.*, **75,** 3935 (1953).
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chains. However, the light scattering results indicate that 0.4 *M* KCl is a better solvent for ionenes than 0.4 *M* KBr, and hence any intermolecular association should decrease in KCl solution. Therefore, the increase in η_{sp}/c is more likely to be a consequence of changes in the extent of binding of the counterions.

The immobilization of dissociated counterions could be due either to the large electrostatic fields which surround macroions (ionic atmosphere binding) or to interaction at specific sites on the polyion (site binding). If the binding process is solely a consequence of coulombic interactions of the counterions with the electrical field of the polyion, then for a series of univalent counterions it is to be expected that ion atmosphere binding would decrease with increasing hydration of the counterion. Hence, counterion binding for the halide ions should decrease in the order $I^- > Br^- > Cl^- > F^-$ (F^- being the most hydrated anion), and this is observed experimentally for the 6,6 Br. Reversal of this type of binding sequence for nucleic acids and polyacrylates with alkali metal counterions, *i.e.*, $K^+ < Na^+ < Li^+$ (Li^+ being the most hydrated cation), has been regarded as evidence for site binding.[16-20]

However, the binding of alkali metal ions to flexible sulfonate polymers has been shown[21] to follow the sequence $K^+ > Na^+ > Li^+$, which is indicative of ionic atmosphere binding, but the cations have been shown to bind to specific $-SO_3^-$ sites. This apparent contradiction is thought to be due to a decrease in the anionic field strength of the charged groups of the polyelectrolyte; *i.e.*, the coulombic energy gained by decreasing the distance between charge centers is small compared to the energy required to desolvate the counterion. Hence, reversal of the purely electrostatic binding order, *e.g.*, nucleic acids and polyacrylates, is indicative of site binding, but the converse, *i.e.*, decrease of binding with increased hydration of counterion, is not conclusive of ionic atmosphere binding. If the experimental binding order is due to site binding, then the solvation energy of the counterion must be the determining factor in the binding selectivity, and desolvation does not occur in the process. Consequently, there sould be no volume changes observed when an ionene solution is mixed with a simple salt solution, as observed for various polymeric acids.[21-23] In order to elucidate this point a dilatometric study is required.

Although most counterion binding studies have been conducted with polyanions, site binding of anions to low molecular weight electrolytes similar to the ionenes has been shown to occur.[24] It might be anticipated that the factors which promote association in these systems will be even more effective in polymeric systems.

It can be seen in Figure 2 that the 6,6 Br is insoluble in 0.4 *M* KI or 0.4 *M* KCNS. This result is in accordance with the counterion binding processes discussed above. Ion atmosphere binding of counterions from the added salt will have the effect of reducing the repulsive forces between dissolved polyions. This repulsive force is directly related to the second virial coefficient, A_2, obtained from light-scattering experiments, and in section C it can be seen that the 6,6 Cl has a lower value of A_2 in 0.4 *M* KBr, compared to 0.4 *M* KCl, indicating that the system is closer to phase separation in KBr solutions.[25]

The experimentally observed counterion binding sequence is therefore $CNS^- > I^- > NO_3^- > Br^- > Cl^- > F^-$, exactly analogous to the sequence observed for the selectivity of strongly basic anion exchange resins, for the same anions.[26] On the basis of the above results it is most likely that 0.4 *M* KNO_3 is closer to the Θ solvent conditions than is 0.4 *M* KBr.

The counterions of the added salt may also interact with specific sites on a polyion, decreasing its effective charge and hence reducing its solubility in water. Solubility in the presence of various added salts will form the basis of further studies.

(B) Light Scattering. Turbidities of unfractionated 3,4 Br and 6,6 Br samples were determined in 0.4 *M* KBr solution, at several polymer concentrations. After being corrected for the solvent contribution, the data were converted into reciprocal specific turbidity, which was then plotted *vs.* polymer concentration. From the above plots, the weight-average molecular weights, $\bar{M}_w$, and the second virial coefficients, A_2, were estimated by means of the Debye equation[27]

$$HC_1/(\tau - \tau_0) = 1/\bar{M}_w + 2A_2C_1 \qquad (9)$$

where τ and τ_0 are the turbidities of solution and solvent, respectively, and C_1 is the concentration of polymer in grams per milliliter. The factor *H* has the value

$$H = \frac{32\pi^3 n^2(dn/dC_1)^2}{3\lambda_0^4 N} \qquad (10)$$

where *n* is the refractive index of the solution, λ_0 is the wavelength *in vacuo* of the light used for the experiment, and *N* is Avogadro's number. Equation 9 has been derived from fluctuation theory for nonionic polymers and is not wholly applicable to the case of charged colloidal particles in a salt solution. Rigorous treatments of light scattering for neutral or charged polymers in multicomponent systems have been given by Brinkman and Hermans,[28] Kirkwood and Goldberg,[29] Stockmayer,[30] Shogenji,[31] Ooi,[32] and Casassa and Eisenberg.[33] A recent application of the fluctuation theory to light scattering by charged particles in salt solutions by Vrij and Overbeek[34] has shown that eq 9 must be written in the form

$$H'C_1/(\tau - \tau^*) = 1/\bar{M}_w + 2A_{2(\mu_s)}C_1 \qquad (11)$$

where τ^* represents the scattering by the mixture of solvent and low molecular weight salt and H' contains a refractive index increment at constant chemical potential, rather than at constant concentration, *i.e.*

$$H' = (32\pi^3 n^2/3\lambda_0^4 N)(\partial n/\partial C_1)^2_{\text{Donnan}} \qquad (12)$$

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where $(\partial n/\partial C_1)_{\text{Donnan}}$ is the refractive index increment measured between the two solutions of a Donnan equilibrium, brought to the same pressure. Membrane equilibrium experiments with ionene polyelectrolytes have indicated that the experimental error due to leakage of low molecular weight polymers through the membrane would probably exceed any correction factor due to a Donnan exclusion effect. Hence it was decided that any attempt to measure $(\partial n/\partial C_1)_{\text{Donnan}}$ was not practicable. However, Vrij and Overbeek[34] have shown that if a refractive index increment at constant salt concentration, $(\partial n/\partial C_1)_{C_2}$, is substituted into eq 12, then an apparent molecular weight, M_1^*, and an apparent second virial coefficient, A_2^*, are found and the relationship between the true molecular weight, M_1, and M_1^* is given by

$$M_1^* = M_1\left[1 + \frac{(\partial n/\partial C_2)_{C_1}}{(\partial n/\partial C_1)_{C_2}}\left(\frac{\partial C_2}{\partial C_1}\right)_{\mu_2}\right]^2 \tag{13}$$

while the relation between A_2 and A_2^* is given by

$$A_2^* = A_2\left[1 + \frac{(\partial n/\partial C_2)_{C_1}}{(\partial n/\partial C_1)_{C_2}}\left(\frac{\partial C_2}{\partial C_1}\right)_{\mu_2}\right]^{-2} \tag{14}$$

Relations equivalent to eq 13 have previously been used by Stockmayer[30] and also by Ooi[32] for mixed solvent systems, while Strauss and Wineman[35] have used an equation equivalent to eq 11 for the determination of the molecular weight of polyphosphates.

If the major contribution to $(\partial C_2/\partial C_1)_{\mu_2}$ is caused by the electrical double-layer adsorption of the supporting electrolyte by the polyelectrolyte, then Vrij and Overbeek have shown that

$$(\partial C_2/\partial C_1)_{\mu_2} = -M_2 Z\alpha/M_1 \tag{15}$$

where M_1 and M_2 are the polyelectrolyte and salt molecular weights, respectively, Z is the number of charges on the polymer chain and $Z\alpha$ represents the negative adsorption of salt and is equal to the difference between the amounts of counterions and co-ions in the electrical double layer. For low potentials, corresponding to high ionic strength of solutions, $\alpha = {}^1/_2$, but for high potentials, corresponding to low ionic strength of solutions, $\alpha < {}^1/_2$. Hence, eq 13 may be written in the form

$$M_1^* = M_1\left[1 - \alpha Z\frac{M_2}{M_1}\frac{(\partial n/\partial C_2)_{C_1}}{(\partial n/\partial C_1)_{C_2}}\right]^2 \tag{16}$$

If $(\partial n/\partial C_2)_{C_1}$ and $(\partial n/\partial C_1)_{C_2}$ are independent of the solution potential, then the correction term in eq 16 will depend upon the value of α, and M_1^* should approach M_1 as the solution potential increases.

A representative 3,4 Br sample was used to determine experimental values of $(\partial n/\partial C_2)_{C_1}$ and $(\partial n/\partial C_1)_{C_2}$ and to examine the effect of solution potential upon these quantities. It was found that $(\partial n/\partial C_2)_{C_1}$ was independent of polymer concentration in the range of concentrations used for the light-scattering measurements. The results are shown in Figure 3. The quantity $(\partial n/\partial C_1)_{C_2}$ was found to be virtually independent of salt concentration except at very low solution potential, *i.e.*, less than 0.1 *M* in salt. The results are given in Table III. It was therefore concluded that the term $(\partial n/\partial C_2)_{C_1}/(\partial n/\partial C_1)_{C_2}$ is constant in the region where KBr concentration is between 0.1 and 0.4 *M*. The apparent molecular weight, M_1^*, was then determined as a function of salt concentration. The results are also shown in Table III and indicate that M_1^* is independent of salt concentration when the latter is greater than 0.2 *M*. Since M_1^* should approach M_1 as the solution potential increases, it has been concluded that in 0.4 *M* KBr solution the Donnan exclusion effect is negligible and that M_1^* is very close to M_1. The variation of A_2^* with salt concentration is shown in Table IV. Although A_2^* does appear to be more dependent upon salt concentration than M_1^*, at the

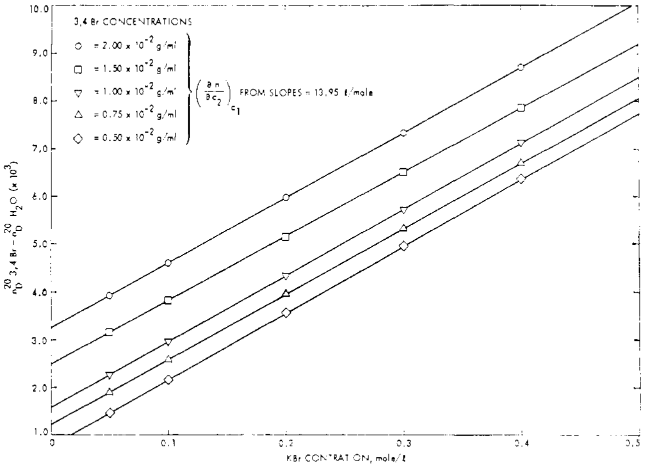

Figure 3. Refractive index of 3,4 Br in aqueous KBr [n^{20}D(3,4 Br)] minus the refractive index of H$_2$O [n^{20}D(H$_2$O)], as a function of KBr concentration.

TABLE III

EXPERIMENTAL VALUES OF $(\partial n/\partial C_1)_{C_2}$, APPARENT MOLECULAR WEIGHT, M_1^*, AND APPARENT SECOND VIRIAL COEFFICIENT, A_2^*, FOR A 3,4 Br SAMPLE, AS A FUNCTION OF KBr CONCENTRATION

KBr concentration, *M*	$(\partial n/\partial C_1)_{C_2}$, ml/g	$M_1^* \times 10^{-4}$	$B^* \times 10^4$
0.40	0.159	6.54	4.42
0.30	0.160	6.40	6.53
0.20	0.160	6.66	10.03
0.10	0.162	6.70	16.10
0.05	0.168	6.90	19.72

TABLE IV

MOLECULAR WEIGHTS AND SECOND VIRIAL COEFFICIENTS

Ionene	Solvent	$[\eta]$, dl/g	d*n*/d*c* × 10	$\bar{M}_w \times 10^{-4}$	$A_2 \times 10^4$
3,4 Br	0.4 *M* KBr	0.162	1.601	3.12	4.16
		0.176	1.564	3.57	4.56
		0.231	1.560	5.78	4.17
		0.250	1.600	6.54	4.42
		0.304	1.597	8.70	4.57
6,6 Br	0.4 *M* KBr	0.155	1.608	1.32	2.30
		0.192	1.588	1.96	2.66
		0.210	1.609	2.27	3.07
		0.319	1.585	4.54	2.81
		0.331	1.567	4.88	2.00
6,6 Cl	0.4 *M* KBr	0.116	1.566	0.86	2.88
		0.150	1.580	1.33	2.65
		0.177	1.546	1.66	2.89
		0.218	1.599	2.44	2.92
6,6 Cl	0.4 *M* KCl	0.145	1.646	1.33	284
		0.179	1.644	1.70	347
		0.242	1.668	2.37	255
		0.290	1.636	2.95	243

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(35) U. P. Strauss and P. L. Wineman, *J. Amer. Chem. Soc.*, **80**, 2366 (1958).

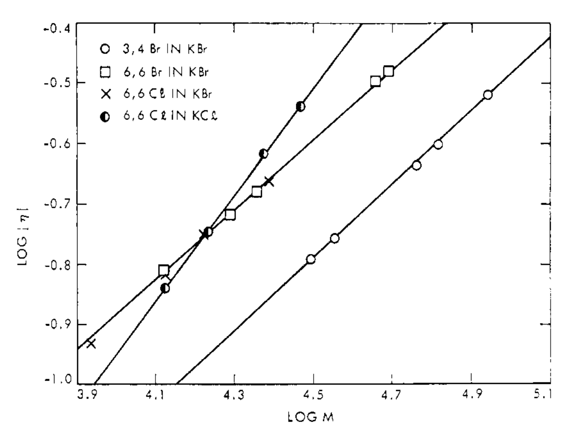

Figure 4. Relationships between intrinsic viscosity and molecular weight, in 0.4 M salt solution.

TABLE V
COMPARISON OF A_2 AND CALCULATED DONNAN TERMS

Ionene	Solvent	A_2(exptl), $\times 10^4$	$1000Z^2/4M^2m_3{}^a$ $\times 10^4$
3,4 Br	0.4 M KBr	4.38	210.0
6,6 Br	0.4 M KBr	2.57	140.0
6,6 Cl	0.4 M KBr	2.83	230.0
6,6 Cl	0.4 M KCl	282.0	230.0

[a] For M = 20,000.

TABLE VI
VISCOSITY AND MOLECULAR WEIGHT RELATIONSHIPS

Ionene	Solvent	K'	a
3,4 Br	0.4 M KBr	2.94×10^{-4}	0.61
6,6 Br	0.4 M KBr	6.22×10^{-4}	0.58
6,6 Cl	0.4 M KBr	6.22×10^{-4}	0.58
6,6 Cl	0.4 M KCl	1.02×10^{-5}	1.00

higher potential (>0.2 M KBr) the variation in A_2^* is quite small. Extrapolation to zero A_2^* of a plot of A_2^* vs. salt concentration indicates that a 0.5 M KBr solution would be a Θ solvent for ionene polyelectrolytes.

In addition, light-scattering measurements were performed in 0.4 M NaBr solution. Vrij and Overbeek[34] have shown that by determining M_1^* in different salt-type solutions and then plotting the square root of M_1^* vs. $M_2(\partial n/\partial C_2)_{C_1}$, a straight line can be obtained. The slope of this plot gives a value of the negative adsorption of salt. Both M_1^* and A_2^* determined in 0.4 M NaBr solution were found to be almost identical with the values determined in 0.4 M KBr solution. Consequently, for the 3,4 Br sample, a plot of $\sqrt{M_1^*}$ vs. $M_2(\partial n/\partial C_2)_{C_1}$ would produce a horizontal straight line, indicating that $M_1^* = M_1$ and that there is no negative adsorption of supporting electrolyte.

As a result of the above evidence, it was concluded that a Donnan exclusion effect was not significant for the case of ionene polymers in 0.4 M KBr solution, and eq 9 may be applied to this system.

Plots of $HC_1/(\tau - \tau_0)$ vs. C_1 were found to be straight lines, and the results are summarized in Table IV. In addition, light-scattering experiments were performed on (a) 6,6 Cl samples using 0.4 M KBr as solvent and (b) the same 6,6 Cl samples using 0.4 M KCl as solvent. These results are also summarized in Table IV. The results shown in Table IV indicate that the specific refractive increments, dn/dC_1, which enter into the constant H in eq 9, are independent of the molecular weights of the samples. The only significant change occurs for the 6,6 Cl in 0.4 M KCl; *i.e.*, dn/dC_1 is dependent to some extent upon the solvent. The slopes of the HC_1/τ vs. C_1 plots were also found to be independent of the molecular weight but varied considerably with change in solvent.

The principal contribution to the second virial coefficient, A_2, for a polyion in which all counterions are dissociated and do not remain within the polyion domain, has been shown to be the Donnan term representing electrostatic repulsion between ions.[36] This term has the value $1000Z^2/4M^2m_3$, where Z is the net charge on the polyion, M is its molecular weight, and m_3 is the added salt molality. Calculated values of the Donnan term for each system investigated are shown in Table V and compared with experimental values of A_2. It is apparent that, except for the 6,6 Cl in 0.4 M KCl, the Donnan term alone, which would have to be added to the excluded volume term, is much larger than A_2. If the domain of the polyion is essentially neutral, the contribution to A_2 due to the excluded volume term should be of the order of 1×10^{-4} for a flexible polymer in the molecular weight range examined.[37] This theoretical value compares very favorably with the experimental values of A_2, except for the 6,6 Cl in KCl.

If the ionene polymers are behaving as essentially neutral polymers in 0.4 M KBr solution, then it might be anticipated that A_2 should decrease as the molecular weight increases. However, only a very narrow molecular weight range has been examined, and any significant change in A_2 due to molecular weight is probably obscured by experimental error.

Intrinsic viscosities, $[\eta]$, were correlated with molecular weight by means of the Mark–Houwink equation

$$[\eta] = K'M^a \quad (17)$$

The parameters K' and a were obtained by plotting log $[\eta]$ vs. log M for each system, shown in Figure 4, and the results are summarized in Table VI.

It was shown in section A that, in the complete absence of salt, $[\eta]$ varies approximately as $M^{2.0}$, indicating the polyions are essentially fully extended rods. In 0.4 M KBr solutions, the ionenes presumably have a random-coil configuration typical of ordinary uncharged polymers. For the 6,6 Cl in 0.4 M KCl, however, a has the value 1.00, indicating some configuration intermediate between the coiled and extended states. This is confirmed by the viscosity results and also by the change in the second virial coefficient, as shown in Table IV. Identical K' and a parameters were obtained for the 6,6 Br and 6,6 Cl samples in 0.4 M KBr, indicating that bromide ions have replaced bound chloride ions, producing essentially a polyion with bromide counterions; *i.e.*, binding is selective towards the bromide ion.

(C) Molecular Dimensions. Unperturbed dimensions of flexible linear macromolecules can be obtained from intrinsic viscosity–molecular weight data, in any solvent, if the hydrodynamic draining effect is negligible and if an estimate can be made of the viscosity expansion factor α_η,[38] defined by

$$[\eta] = KM^{1/2}\alpha_\eta{}^3 \quad (18)$$

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(36) C. Tanford, "Physical Chemistry of Macromolecules," Wiley, New York, N. Y., 1961, Chapter 4.

(37) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

(38) P. J. Flory and T. G. Fox, Jr., *J. Amer. Chem. Soc.*, **73**, 1904 (1951).

Stockmayer and Fixman have shown[39] that eq 18 can be written in the form

$$[\eta] \cong KM^{1/2} + 0.51\Phi BM \qquad (19)$$

where Φ is the Flory–Fox "constant" and B is the polymer–solvent interaction parameter. Hence, a plot of $[\eta]M^{-1/2}$ *vs.* $M^{1/2}$ should produce a straight line with ordinate intercept equal to K. Equation 19 was applied to the systems investigated, using the data given in Table IV, and the results are shown in Table VII.

The unperturbed dimensions of the chain are then obtained from

$$K = \Phi A^3 \qquad (20)$$

where

$$A^2 = \langle L_s^2\rangle_0 M^{-1} \qquad (21)$$

and where L is the end-to-end distance.

Chain dimensions (but not "unperturbed" values) can be obtained directly from the intrinsic viscosity values by means of the equation[25]

$$[\eta] = \Phi\langle L_v^2\rangle^{3/2}M^{-1} \qquad (22)$$

Values of L, for the 3,4 Br and 6,6 Br samples in 0.4 *M* KBr, determined from eq 20 and 22, are compared in Table III. The value of Φ was taken to be 2.1×10^{21}, which has previously been proposed[40] for heterodisperse polymers. Table VIII shows good agreement between values of L_s and L_v and reflects the small deviations of α_η (eq 18) from unity.

The theoretical root-mean-square end-to-end distance of an unbranched, uncharged polymer molecule of n links, each of length l, with a fixed valence angle α between successive bonds and free internal rotation about each bond, is given by the expression[41]

$$L_f = ln^{1/2}[(1 + \cos\alpha)/(1 - \cos\alpha)]^{1/2} \qquad (23)$$

For ionene polymers, the average bond length is 1.52 Å, α is approximately 71°, and $n = (M/M_0)b$, where M_0 is the unit molecular weight and b is the number of chain bonds per unit. Calculated values of L_f are shown in column 5 of Table VIII. A measure of the flexibility of the polymer chain can now be obtained by taking the ratio L_s/L_f, and these values are shown in the last column of Table VIII. The value of 2.1 indicates considerable hindrance to free rotation, due presumably to the bulky methyl groups on each N atom in the chain, but is comparable to that of polystyrene and polyisobutylene.[25]

TABLE VII
STOCKMAYER–FIXMAN PARAMETERS[a]

Ionene	Solvent	$0.51\Phi B$ $\times 10^6$	K $\times 10^4$
3,4 Br	0.4 *M* KBr	0.72	7.92
6,6 Br	0.4 *M* KBr	1.48	11.74

[a] Results have not been included for the 6,6 Cl in 0.4 *M* KCl, since the Stockmayer–Fixman relation is not applicable[42] for a system where a (eq 17) = 1.

TABLE VIII
CALCULATED VALUES OF L FOR 3,4 Br AND 6,6 Br SAMPLES IN 0.4 *M* KBr SOLUTION

Ionene	Mol wt	L, Å L_s	 L_v	 L_f	L_s/L_f
3,4 Br	3.12	128	140	61	2.10
	3.57	136	144	65	2.09
	5.78	174	185	83	2.10
	6.54	185	198	89	2.08
	8.70	213	233	102	2.08
6,6 Br	1.32	95	103	45	2.11
	1.96	115	121	55	2.09
	2.27	124	131	59	2.10
	4.54	176	190	84	2.10
	4.88	182	197	87	2.09

The effect on L of varying the charge density in the polymer backbone can be estimated by rewriting eq 20 in the form

$$\langle L^2\rangle = (K/\Phi)^{2/3}M_b n \qquad (24)$$

where M_b is the molecular weight per bond and n is the number of bonds in the polymer chain. Hence, it is possible to compare the 3,4 Br and 6,6 Br ionenes, with equal values of n, by means of the following expression

$$\frac{\langle L^2\rangle_{3,4}}{\langle L^2\rangle_{6,6}} = \left(\frac{K_{3,4}}{K_{6,6}}\right)^{2/3}\frac{M_{b_{3,4}}}{M_{b_{6,6}}} \qquad (25)$$

For the 3,4 Br, $M_b = 38.4$, while for the 6,6 Br, $M_b = 29.7$. Using the values of K given in Table VII

$$\langle L^2\rangle_{3,4}/\langle L^2\rangle_{6,6} = 0.992$$

This result indicates that variation of the charge density in the polymer chain has no significant effect upon L when 0.4 *M* KBr is the solvent. This appears to confirm the suggestion that the ionene polymers are essentially neutral in this solvent.

Conclusions

The following conclusions may be drawn from the results shown above. (1) In the absence of added salts, the viscosity behavior of ionene polyelectrolytes is accurately represented by the Fuoss equation,[6] and the polyions have a stiff rodlike configuration. (2) In the presence of 0.4 *M* KBr solution, the viscosity behavior is similar to that of uncharged polymers. (3) Counterion binding appears to increase in the order $F^- < Cl^- < Br^- < NO_3^- < I^- < CNS^-$, similar to that observed for strongly basic anion exchange resins. (4) The intrinsic viscosity–molecular weight relationships, for unfractionated samples in 0.4 *M* KBr solution, are $[\eta] = (2.94 \times 10^{-4})M^{0.61}$ for the 3,4 Br and $[\eta] = (6.22 \times 10^{-4})M^{0.58}$ for the 6,6 Br. (5) Variation in the charge density of the polymer chain does not appear to effect the root-mean-square end-to-end distance in 0.4 *M* KBr solution.

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[39] W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, No. **1**, 137 (1963).

[40] S. Newman, W. R. Krigbaum, C. Laugier, and P. J. Flory, *ibid.*, **14**, 451 (1954).

[41] H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

[42] P. J. Flory, *Makromol. Chem.*, **98**, 128 (1966).