For most of the compounds studied in the present investigation, not enough detailed measurements were made to attempt a more complete interpretation of such curves.[4] However, some observations on desorption potentials, as determined from the positions of the adsorption–desorption peaks, are of interest in connection with the question of the importance of adsorption as a possible step in electroreduction mechanisms. If the desorption potentials of the original compound and its reduction product are reached at a lower cathode potential than the reduction potentials, it seems clear that adsorption cannot play a role in the reduction mechanism. Thus acetophenone in millimolar concentrations in 0.1 *M* sodium perchlorate is desorbed at a potential of about -1.1 v. (*vs.* S.C.E.), its first reduction product acetophenone pinacol at about -1.3 v., while reduction in a neutral unbuffered solution does not begin until about -1.5 v.[13] Even in a buffered solution of *p*H 4.6, the half wave potential is -1.35 v.[14] Apparently, adsorption does not play a role in the reduction mechanism.

Likewise, ethyl benzoate and its reduction product benzyl alcohol are desorbed at -1.1 and -1.0 v., respectively, in 0.1 *M* sodium perchlorate, as compared to the half-wave potential of -2.14 v. in 0.05 *N* tetraethylammonium iodide solution in 75% dioxane.[15]

Chlorobenzene was not found to exhibit measurable surface active behavior, 10^{-3} *M* bromobenzene barely showed a noticeable effect on the double layer capacity of 0.1 *M* sodium perchlorate, while 10^{-3} *M* iodobenzene gave a saturated monolayer. However, desorption of iodobenzene occurred at about -1.3 v., which is anodic with respect to its reduction potential.[16] Therefore adsorption seems to play no role in the reduction.

Di-*n*-propyl ketone and diisopropyl ketone, which are weakly surface active, are desorbed far below their reduction potentials.

In contrast, the first reduction step of 1,10-phenanthroline occurs at a half-wave potential[17] of -1.23 v., and adsorption occurs on both sides of this potential, indicating that both oxidized and reduced forms are strongly surface active. Not enough is known about the reduction process, however, to make it worth while to speculate about the possible role of adsorption.

Alizarin Red S showed a strong pseudocapacity behavior in the region of its half-wave potential (-0.45 v. in an acetate buffer of *p*H 4.73)[18] and marked capacity minima on both sides of the half-wave potential, a behavior characteristic of a reversible reduction step with adsorption of both oxidized and reduced forms.

A similar pseudocapacity behavior was observed for methylene blue in an acetate buffer. A strong capacity minimum was observed on the cathodic side (-0.6 v.), corresponding to a marked adsorption of the reduced form. Brdicka[19] and Müller[20] have clearly demonstrated from polarographic observations that the adsorption prewave is characterized by the formation of a monolayer of adsorbed reduction product. The present result demonstrates unequivocally that an adsorbed layer of reduction product is also formed at more cathodic potentials.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS, THE STATE UNIVERSITY]

Molecular Dimensions and Interactions of Long-chain Polyphosphates in Sodium Bromide Solutions[1]

BY ULRICH P. STRAUSS AND PHILIP L. WINEMAN

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Light scattering and viscosity investigations were carried out in aqueous sodium bromide solutions at 25° on samples of sodium polyphosphate whose molecular weights ranged from 11,000 to 1,250,000. Most of the samples were prepared from potassium Kurrol salts by ion exchange; a few were Graham salts. For molecular weights above 70,000, intrinsic viscosity–molecular weight relationships in 0.35 and 0.415 *M* NaBr were $[\eta] = 0.65 \times 10^{-4} M^{0.69}$ and $[\eta] = 4.94 \times 10^{-4} M^{0.50}$, respectively. At lower chain lengths, the exponent of *M* became smaller in both solvents. From a study of one sample in solutions of several NaBr concentrations, the 0.415 *M* solution was also found to be the one in which the second virial coefficient vanishes. The proportionality of the intrinsic viscosity to the square root of the molecular weight in the same solvent in which the second virial coefficient vanishes is predicted by Flory's theory but apparently has not been demonstrated previously for a polyelectrolyte. The ratio of the molecular dimensions in this theta-solvent to those calculated assuming free rotation about each P–O bond is 1.68 which is close to the corresponding value reported for a silicone but smaller than values obtained with most polymers based on the carbon chain. Theoretical relationships between the second virial coefficient and molecular dimensions are obeyed by sodium polyphosphate to about the same extent as they are by uncharged high polymers. However, the ionic strength dependence of the molecular dimensions could not be fitted to existing theories. The assumptions underlying Flory's equation were examined by an alternate derivation. Other theories could not be applied because of the strong solvent incompatibility of un-ionized $NaPO_3$ groups, which made extrapolation of the molecular dimensions to infinite ionic strength meaningless.

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Despite a large number of investigations in recent years, the properties of polyelectrolytes are still not well understood. It becomes increasingly clear that in order to obtain such an understanding it is necessary to determine and correlate a large number of properties of a given polyelectrolyte system in a much more comprehensive manner than has been done to date. For reasons previously stated[2] the inorganic long chain polyphosphates are well suited for this purpose. This paper describes a part of such a comprehensive study, covering light scattering and viscosity studies in sodium bromide solutions.

By ion exchange of potassium Kurrol salts, sodium polyphosphate samples of much higher molecular weights than the previously investigated Graham salts[2] were prepared, and in this way a molecular weight range could be studied in which existing theories concerning polymer behavior have proved successful. In particular, this study was aimed at (1) obtaining information concerning the unperturbed molecular dimensions and the solvent interactions of the polyelectrolyte; (2) examining relations between molecular dimensions, second virial coefficients and the sodium ion concentration; and (3) obtaining molecular weight–intrinsic viscosity relationships which would be useful for future determination of molecular weights from viscosity data.

Experimental

Sodium Polyphosphate.—Samples NaPP 2-119, 6-13 and 6-12 were Graham salts prepared as previously described[2] from $NaH_2PO_4 \cdot H_2O$ whose Na/P ratio had been adjusted to unity with Na_2CO_3. All other sodium polyphosphate (NaPP) samples were prepared as follows. Potassium Kurrol salts were prepared, with slight modifications, by the method of Pfanstiel and Iler.[3] Batches of KH_2PO_4, whose K/P ratio had been adjusted to 1.001, were heated in a platinum dish at constant temperature within the range 300–700° for from 1 to 100 hr., followed by rapid cooling by floating the dish in cold water. Water-soluble low molecular weight impurities were then removed as described.[3] The Kurrol salts were then converted to sodium polyphosphate by batchwise ion exchange with a resin containing sodium sulfonate groups (Nalcite HCR-12, 200–400 mesh), followed by filtration and removal of the water by freeze-drying between 10^{-4} and 10^{-3} mm. The white, porous, spongy products contained from 6.6 to 8.9% water, as determined by the weight loss after heating to constant weight at 700°. The samples were analyzed for phosphorus content by potentiometric titration with sodium hydroxide of the orthophosphate solutions formed by boiling the polyphosphate in dilute nitric acid. The samples were also analyzed for residual potassium ion with a Perkin-Elmer flame photometer, using an internal-standard procedure.[4] Except for samples 5D, 6, 6D and 6DD which contained close to 6 meq. K^+ per 100 meq. of phosphate, the samples contained about one meq. K^+ per 100 meq. of phosphate. With the meq. Na^+ calculated from the difference between meq. phosphate and meq. K^+, the sum of all the analyses accurately accounted for the sample weight to within 5 parts per 1000 in each case, indicating that the samples contained insignificant amounts of non-volatile constituents other than those known to be present. To minimize degradation by the residual water, the samples were kept close to 0° in a refrigerator. Since the object of this work was to correlate light scattering and viscosity results, the effects of degradation, both in and out of solution, were kept negligible by performing all solution preparations and measurements on a given sample–solvent system within 12 hr.

Light Scattering.—Light scattering measurements were performed at 25° in a Brice–Phoenix photometer,[5] using incident unpolarized monochromatic light of wave lengths of 4360 and 5460 Å. The measurements were carried out in semi-octagonal cells of 40 mm. width with solutions or solvents which had been filtered through sintered glass filters of "ultrafine" porosity. All dissymmetry measurements were corrected for back-reflection of the incident light.[6]

The photometer was calibrated with the opal glass standard diffusor of known opacity furnished by the manufacturer. A 0.5% toluene solution of a standard polystyrene sample, kindly furnished by Professor P. Debye of Cornell University, had excess Rayleigh ratios[7] of 2.08 × 10^{-4} and 0.84 × 10^{-4} at 4360 and 5460 Å., respectively, which agree closely with values reported by other investigators.[5,8]

Refractive index differences between solutions and solvents were measured in a Brice–Phoenix differential refractometer which was calibrated by means of sucrose solutions.[9]

Viscosity.—A Bingham viscometer[10] (our No. 9) operating at driving pressures from 20 to 160 g./cm.² was used to measure viscosities at 25.00°. The viscometer was calibrated with sucrose solutions by the method of Fuoss and Cathers,[11] so that observed pressure–flow time products, *pt*, could be corrected for kinetic energy and drainage effects. The viscometer constant for water, $(pt)_0$, was 6760 g. sec./cm.². In the few instances where a slight shear dependence was noticeable, corrections were made by extrapolation to zero velocity gradient.

Results and Discussion

Molecular Weight–Intrinsic Viscosity Relationships.—The light scattering results for the three-component system *water* (component 1), *sodium polyphosphate* (component 2) and *sodium bromide* (component 3) are given by the equations[12,13]

$$\frac{K_L c_2}{R_{90}} = \frac{1}{(1 - D)^2}(A + 2Bc_2) \qquad (1)$$

$$K_L = 2\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c_2)^2 / N_A \lambda^4 \qquad (2)$$

$$D = \frac{(\partial n/\partial c_3)}{(\partial n/\partial c_2)} \times \frac{M_3}{M_2} \times \frac{a_{23}}{a_{33}} \qquad (3)$$

$$M_2 = \frac{1}{A} \times \frac{1}{P(90)} \times \frac{6 - 7\rho_u}{6 + 6\rho_u} \qquad (4)$$

In these equations, R_{90} is the excess Rayleigh ratio of the solution over that of the solvent, c_j is the concentration of component j in grams per ml., n is the refractive index of the solution, N_A is Avogadro's number, λ is the wave length of the light, M_j is the molecular weight of component j, $a_{jk} = (1/RT) \times (\partial \mu_j / \partial m_k)$ where μ_j and m_j are the chemical potential and molarity, respectively, of component j, ρ_u is the depolarization[14] and $1/P(90)$ is the dissymmetry correction, obtained from the intrinsic dissymmetry, $[Z]$, by using the tables of Doty and

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[6] A. Oth, J. Oth and V. Desreux, *J. Polymer Sci.*, **10**, 551 (1953).

[7] The Rayleigh ratio, R_{90}, is defined by the relation $R_{90} = r^2 i_{90}/I_0$ where I_0 is the intensity of the incident light and i_{90} is the intensity of the scattered light per unit volume at 90° and at a distance r.

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[9] C. A. Browne and F. W. Zerban, "Physical and Chemical Methods of Sugar Analysis," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 1206.

[10] E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, N. Y., 1922.

[11] R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, **4**, 97 (1949).

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[13] W. H. Stockmayer, *ibid.*, **18**, 58 (1950).

[14] The depolarization correction in equation 4 was made in all cases, but because the values of ρ_u were smaller than 0.025 they are not reported here.

TABLE I

LIGHT SCATTERING AND VISCOSITY RESULTS OF NaPP-7 IN SEVERAL SODIUM BROMIDE SOLUTIONS

m_3	$1/(1 - D)^2$	$\frac{\partial n}{\partial c_2}$	$B \times 10^{4\,a}$	[Z] 4360 Å.	[Z] 5460 Å.	$M_2 \times 10^{-3\,a}$	[η] (dl./g.)	R_w(Å.) from $[Z]^a$	R_w(Å.) from $[\eta]^b$	$B \times 10^4$ (theor.)^c
0.10	1.28	0.109	10.2	1.90	1.60	670	2.76	1110	970	8.8
.25	1.36	.105	4.2	1.50	1.32	700	1.24	790	740	2.2
.35	1.41	.102	1.5	1.35	1.25	690	0.72	660	620	0.6
.40	1.42	.101	0.4	1.29	1.22	690	0.50	610	550	0.1

[a] Averages of 4360 and 5460 Å. values. [b] Calculated by equation 7 with $M_2 = 690{,}000$ and $\phi' = 2.1 \times 10^{21}$. [c] Calculated by equation 9.

TABLE II

LIGHT SCATTERING AND VISCOSITY RESULTS OF SEVERAL SAMPLES OF SODIUM POLYPHOSPHATE

$n_0(4360) = 1.345$, $n_0(5460) = 1.339$, $\frac{\partial n}{\partial c_2} = 0.102$, $K_L(4360) = 16.9 \times 10^{-8}$, $K_L(5460) = 6.75 \times 10^{-8}$

Sample no.	$B \times 10^{4\,a}$	$[Z]^a$ 4360 Å.	$[Z]^a$ 5460 Å.	$M_2 \times 10^{-3\,a}$	[η](dl./g.) in 0.35 M NaBr	[η](dl./g.) in 0.415 M NaBr	R_w(Å). in 0.35 M NaBr from [Z]	R_w(Å). in 0.35 M NaBr from $[\eta]^c$
2-119	2.1	..	..	11	0.061	0.059	..	..
6-13	1.4	..	..	24	.087	.081	..	..
6-12	1.7	..	..	34	.101	.093	..	..
5D	1.7	..	..	44	.120	...	..	..
2D	1.7	..	..	62	.141	...	..	..
3D	1.7	..	..	111	.195	...	..	..
3	1.7	..	..	123	.213	...	..	..
1D	..	..	..	157^b	.249	.194	..	..
6DD	1.2	1.18	1.13	249	.326	.240	465	340
6D	..	..	..	250^b	.344	.242	..	..
7D	..	..	..	388^b	.466	.310	..	..
6	1.6	1.28	..	420	.472	...	575	455
8DD	1.4	1.38	1.28	690	.63	.407	705	590
7	1.5	1.35	1.25	690	.72	...	660	620
8D	..	..	..	765^b	.75	.505	..	..
8	0.9	1.71	1.47	1250	1.05	...	970	855

[a] All light scattering results refer to 0.35 M NaBr as the solvent. Except in the case of [Z], averages of 4360 and 5460 Å. results are given. [b] Determined from equation 5. [c] Calculated by equation 7 with $\phi' = 2.1 \times 10^{21}$.

Steiner.[8] The values of [Z] were obtained from plots of $1/(Z - 1)$ against c_2, where Z is the dissymmetry due to the polymer measured at finite polymer concentrations.

In order to calculate D, the quantity (a_{23}/M_2a_{33}) was found by membrane equilibrium measurements[15] to vary from 0.87×10^{-3} in 0.10 M NaBr to 1.15×10^{-3} in 0.40 M NaBr. The refractive increments of the polyelectrolyte are given in Table I, while $\partial n/\partial c_3$ was interpolated from literature values[16-18] to be 0.138. The quantity $1/(1 - D)^2$ then ranges from 1.28 to 1.42 as shown in Table I.[19]

The data are summarized in Tables I and II. The values of M_2 and of B obtained at 4360 and 5460 Å. were in respective agreement, and therefore only the mean values are reported in these tables. Results for one sample in several solvents differing in sodium bromide molarity are compared in Table I. The values of M_2 vary somewhat, but this variation may be within the limits of experimental error. By extrapolating a plot of B against m_3, one finds that $B = 0$ in 0.415 M NaBr.

The results obtained with a large number of samples covering a hundred-fold molecular weight range are compared in Table II. All the light scattering results were obtained in 0.35 M NaBr. Intrinsic viscosities were determined in the same solvent and in many cases also in 0.415 M NaBr. While most molecular weights were determined directly by light scattering, in a few instances the molecular weights were determined from the intrinsic viscosity values in 0.35 M NaBr by interpolation of the known relationship between [η] and M_2 in that solvent.

The dependence of log [η] on log M_2 in 0.35 and 0.415 M NaBr is shown in Fig. 1 by curves 1 and 2, respectively. For molecular weights above about 70,000, the data are well represented by straight lines, leading to the equations

$$[\eta] = 0.65 \times 10^{-4} M_2^{0.69} \text{ (in 0.35 } M \text{ NaBr)} \qquad (5)$$

$$[\eta] = 4.94 \times 10^{-4} M_2^{0.50} \text{ (in 0.415 } M \text{ NaBr)} \qquad (6)$$

In the lower molecular weight region the lines become less steep. This result does not conform with currently available hydrodynamic theories[20,21] which predict an increase in the slope as the chain

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(15) U. P. Strauss, P. Ander and M. Levy, unpublished data.

(16) G. P. Baxter, A. C. Boylston, E. Mueller, N. H. Black and P. B. Goode, THIS JOURNAL, **33**, 901 (1911).

(17) W. Geffcken and D. Price, *Z. physik. Chem.*, **26B**, 81 (1934).

(18) C. Bender, *Wied. Ann.*, **39**, 89 (1890).

(19) In the absence of membrane equilibrium data, D had been assumed negligible in a previous study.[2] With the correct value of $1/(1 - D)^2$ and in view of a 10% difference in instrument calibrations, the molecular weights reported in the previous paper should be multiplied by 1.54 to bring them in line with the values reported here. This procedure also raises the ratio of light scattering to end-group molecular weights, reported by Strauss and Treitler, closer to the theoretical value of 2, and changes the formula relating light scattering molecular weight to intrinsic viscosity of Graham salts in 0.035 M NaBr to $M_w = 1.0 \times 10^6$ ([η] − 0.025) (U. P. Strauss and T. L. Treitler, THIS JOURNAL, **77**, 1473 (1955)).

(20) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

(21) P. Debye and A. M. Bueche, *ibid.*, **16**, 573 (1948).

length decreases and the molecule becomes more permeable to the solvent.[22] Although the three samples of lowest molecular weight are Graham salts, whereas the remainder of the samples originated from Kurrol salts, curve 1 shows that the change of slope is not due to possible structural differences between these two kinds of compounds. The break occurs clearly in the Kurrol salt region. Furthermore, the change of slope is not a polyelectrolyte effect, for a similar effect has been reported for polystyrene in benzene.[23] Actually, such a change of slope is necessitated if the curves are to be extrapolated smoothly to the molecular weight of the monomer for which one would expect the intrinsic viscosity to be close to the Einstein value for spheres. Linear extrapolation of most of the reported log $[\eta]$-log M relationships would lead to monomer intrinsic viscosity values which are too low.

Equation 6 shows that in 0.415 M NaBr, in which the second virial coefficient has been demonstrated to vanish, the intrinsic viscosity is proportional to the square root of the molecular weight. This relationship, which is predicted by Flory's theory[24] and amply confirmed by experiment for non-ionogenic polymers, has apparently not previously been demonstrated for a polyelectrolyte. Thus we may consider the 0.415 M NaBr solution a theta-solvent. This conclusion is further strengthened by the observation that phase separation of a high molecular weight polyphosphate occurred at a sodium bromide molarity of 0.47.[25]

Molecular Dimensions and Second Virial Coefficient.—Values of the root-mean-square end-to-end distance, R, determined from light scattering dissymmetry and from intrinsic viscosity are compared in Tables I and II. Since the polyphosphate samples were not fractionated, weight average values were calculated assuming the *Most Probable Distribution* of molecular weights.[26] The light scattering R_w values could then be obtained directly from the intrinsic dissymmetry using the *polydisperse coil* tabulations of Doty and Steiner.[8] The intrinsic viscosity R_w values were obtained from the equation

$$R_w^3 = \frac{[\eta]M_2}{\phi'} \quad (7)$$

by following a procedure similar to that used by Newman, *et al.*,[27] where ϕ' can be shown to be about 10% less than the value of ϕ for monodisperse polymers. Consequently, we took ϕ' equal to $2.1 \times 10.^{21}$ The quantity M_2, being obtained from light scattering measurements, is a weight-average value. In general the light scattering values are larger than the viscosity values. The differences may be due to experimental uncertainty in the dissymmetry data and to possible deviations of the actual molecular weight distribution of the samples from the assumed one.

Flory and Fox[28] have shown that in a theta-solvent the molecular dimensions are unperturbed by long-range interactions and are therefore characteristic of the intrinsic flexibility of the polymer molecule. In such a solvent, we have the relation

$$K = \phi'(R^2{}_{wo}/M_w)^{3/2} \quad (8)$$

where $K = [\eta]/M_w{}^{0.50}$. R_{wo} is the unperturbed R_w and M_w is the weight-average molecular weight. From the value of 4.94×10^{-4} for K,[29] we calculate $(R_o{}^2/M)^{1/2}$ [30] to be 620×10^{-11}. If we denote by R_{of} the unperturbed root mean square end-to-end distance calculated for the hypothetical case of free rotation about each bond in the polyphosphate chain, we find the quantity $(R^2{}_{of}/M)^{1/2}$ to be 370×10^{-11}, assuming a P–O bond length of 1.59 Å., and the P–O–P and O–P–O angles equal to 129°[31] and 109.5°, respectively.[32] The ratio R_o/R_{of} becomes 1.68 which is very close to the corresponding value of 1.60 for polydimethylsiloxane but smaller than the values for polyacrylic acid (1.96) and polystyrene (2.44).[33,34] Because of the oxygen with its wide valence angle in the chain, there seems to be less steric hindrance and hence greater flexibility in the polyphosphates and silicones than in the polymers based on single-bond carbon chains.

The relation between the molecular dimensions and the second virial coefficient is of interest. It can be shown that the theory of Flory and Fox[28] gives the following relationship between B and α, the linear expansion coefficient defined as $([\eta]/[\eta]_\theta)^{1/3}$, $[\eta]_\theta$ being the intrinsic viscosity in the theta-solvent[35]

$$B = (2\pi/9)^{3/2}N_A(R_0{}^2/M)^{3/2}[(\alpha^5 - \alpha^3)/M^{1/2}]F(X) \quad (9)$$

where the quantity $F(X)$ is a slowly varying function[36] which in our case has values between 0.56 and 0.97 if X is taken to be equal to $2(\alpha^2 - 1)$.[37] The values of B, calculated by equation 9 for sample NaPP-7 are presented in the last column of Table I. Comparison with the observed values of B in the third column of this table shows improved agreement with increasing values of B. This behavior also has been observed with poly-4-vinylpyridine.[38] The value of $[\eta]_\theta$, needed for the cal-

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(22) Probable causes for the failure of these theories in the low molecular weight region have been discussed recently (M. L. Hunt, S. Newman, H. A. Scheraga and P. J. Flory, *J. Phys. Chem.*, **60**, 1278 (1956)).

(23) W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, **11**, 37 (1953).

(24) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chs. 12–14.

(25) U. P. Strauss, D. Woodside and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).

(26) Ref. 24, Ch. 8.

(27) S. Newman, W. R. Krigbaum, C. Laugier and P. J. Flory, *J. Polymer Sci.*, **14**, 451 (1954).

(28) P. J. Flory and T. G. Fox, THIS JOURNAL, **73**, 1904, 1909, 1915 (1951).

(29) See equation 6.

(30) It is clear that $R_{wo}{}^2/M_w = R_o{}^2/M$.

(31) D. E. C. Corbridge, *Acta Cryst.*, **9**, 308 (1956).

(32) For details concerning the method of calculation, see ref. 24, p. 420.

(33) Ref. 24, p. 618.

(34) A considerably larger value has been reported for a lithium polyphosphate sample in 0.4 M lithium chloride solution (G. Saini and L. Trossarelli, *J. Polymer Sci.*, **23**, 563 (1957)). If true, this would indicate that the cation has a large effect on the chain flexibility. However, phase separation studies[25] suggest that the molarity at which aqueous LiCl becomes a theta-solvent is much higher than 0.4 and that therefore the chain is expanded in 0.4 M LiCl by long range interactions. Further investigation of this problem is in progress.

(35) N. S. Schneider and P. Doty, *J. Phys. Chem.*, **58**, 762 (1954).

(36) Ref. 24, p. 528.

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

(38) A. G. Boyes and U. P. Strauss, *J. Polymer Sci.*, **22**, 463 (1956).

culation of α, was obtained from the empirical equation

$$[\eta] = 0.41 + 2.02 \times 10^3 B \qquad (10)$$

which represents the $[\eta]$ and B data of NaPP-7 in 0.25, 0.35 and 0.40 M NaBr. Two observations are of interest. First, if one divides 0.41, the value $[\eta]_\theta$, by the square root of the molecular weight, one obtains a value of K of 4.94×10^{-4}. This value which is based on determinations of one sample in several solvents is identical with the value which was obtained from a large number of samples in one solvent. Second, Krigbaum has recently shown that a linear relation between $[\eta]$ and B theoretically should be, and actually is, satisfied by high polymers near the theta point.[39] The coefficient of B in equation 10 which would be expected on theoretical grounds is 2.9×10^3, which is about 50% higher than the experimental value. The discrepancy is somewhat larger than, but not too much out of line with, similar differences reported for a number of ordinary high polymers.[39]

Molecular Dimensions and Electrolyte Concentration.—The foregoing discussion shows that sodium polyphosphate follows the same theoretical relations between molecular weight, intrinsic viscosity and second virial coefficient which are usually observed for uncharged high polymers. This does not, however, imply that the charge of these polyelectrolytes is near zero, for electrophoresis experiments indicate 30–40% ionization over the range of NaBr molarities investigated here.[25] It remains to examine the dependence of the molecular dimensions[40] on the electrolyte concentration in terms of existing theories. Attempts to apply the Hermans–Overbeek theory[41] immediately reveal a fundamental difficulty. This theory expresses the molecular expansion relative to the molecular dimensions at infinite ionic strength where the effects of electrical charge are assumed to be completely screened out. On performing the required extrapolation of an R^2 against $m_3^{-1/2}$ plot with relevant data in Table I, one finds the value of R^2 at infinite ionic strength to be negative, leading to a physically impossible value for R. The difficulty cannot be avoided by using the molecular dimensions in the theta-solvent instead of those at infinite ionic strength for the calculation of the expansion. for electrophoresis indicates that at the theta point the electrical charge is far from the zero value necessary for the application of the theory. The same difficulty is encountered with other theories which require finite or, even more restrictively, unperturbed random coil molecular dimensions at infinite ionic strength.[42–44]

Flory's theory[45] does not suffer from this disadvantage and can be tested with our data. His equation may be expressed in the form

$$(\alpha^5 - \alpha^3)/M^{1/2} = f + 2C_\text{I} i^2/m_3 \qquad (11)$$

where

$$C_\text{I} = (3^3 \times 10^3/2^{9/2}\pi^{3/2})N_\text{A}^{-1}M_0^{-2}(R_0^2/M)^{-3/2} \qquad (12)$$

and i is the number of electronic charges per polymer unit of molecular weight M_0. The first term corresponds to the interactions between the solvent and the (hypothetical) uncharged polymer. In Fig. 2, a plot of $(\alpha^5 - \alpha^3)/M^{1/2}$ against $1/m_3$ for sample NaPP-7 using the viscosity data in Table I is seen to be linear. The slope of the line is 2.79×10^{-3}. Setting M_0 equal to 102, the molecular weight of one (NaPO_3) unit, the value of C_I, calculated by equation 12, is 0.143. Thus, with $i = 1$, the theoretical slope in equation 11 is more than 100 times the experimental one. With the average electrophoresis value of 0.35 for i,[25] the discrepancy still amounts to more than an order of magnitude. To reach agreement, i would have to be taken equal to 0.10. One might feel tempted to consider this value the "effective thermodynamic degree of ionization." However, if one interprets the Donnan membrane equilibrium results[15] in a similar manner, *e.g.*, by lumping all deviations from ideality into an effective degree of ionization, one finds i to be near 0.20. Thus, there is no unique "thermodynamic charge" in terms of which all the data can be interpreted. The situation is similar to that which existed with respect to simple electrolytes before the advent of the Debye–Hückel theory, when it was impossible to explain the incomplete osmotic activity of strong electrolytes in terms of the Arrhenius ionization theory.

Some insight into the assumptions underlying equation 11 can be obtained by a derivation different from Flory's. If one defines the polyelectrolyte component so that iP of its P phosphate groups are ionized and the remaining $(1 - i)P$ groups un-ionized, then the second virial coefficient can be expressed by the relation

$$B = \frac{1000}{2M^2}\left\{\frac{(iP)^2}{m_3} + \beta_{22} - \frac{m_3[(iP/m_3) + \beta_{23}]^2}{2 + \beta_{33}m_3}\right\} \qquad (13)$$

where $\beta_\text{jk} = \partial \ln \gamma_\text{j}/\partial m_\text{k}$, γ_j being the activity coefficient of component j. By eliminating B between equations 9 and 13, one obtains

$$(\alpha^5 - \alpha^3)/M^{1/2} = \frac{4C_\text{I}}{F(X)}\left\{\frac{i^2}{m_3} + \frac{\beta_{22}}{P_2} - \frac{m_3[(i/m_3) + (\beta_{23}/P)]^2}{2 + \beta_{33}m_3}\right\} \qquad (14)$$

where C_I is defined by equation 12 Equation 14 can now be reduced to equation 11 if one approximates $F(X)$ by unity and makes the assumptions that β_{23} and β_{33} are equal to zero and β_{22} is independent of m_3. In general, β_{22} depends on both the solvent affinity of the polymer in its un-ionized state and the osmotic effectiveness of the ionized counterions, and therefore one would expect it to vary with m_3. Similarly, β_{23} and β_{33} are not generally zero. The incorrectness of these assumptions then accounts for the quantitative failure of equation 11. Nevertheless, it is clear that the derivation of equations 14 and 11 does not necessitate a detailed molecular polyelectrolyte model but can be performed with the phenomenological equation 13 together with equation 9 which is a general expression of the equivalence of intramolecular and intermolecular segment–segment interactions.

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(39) W. R. Krigbaum, *J. Polymer Sci.*, **18**, 315 (1955).

(40) In view of relation (9), a similar examination of the second virial coefficient would be equivalent.

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

(42) W. Kuhn, O. Künzle and A. Katchalsky, *Helv. Chim. Acta*, **31**, 1994 (1948).

(43) A. Katchalsky and S. Lifson, *J. Polymer Sci.*, **11**, 409 (1953).

(44) S. A. Rice and F. E. Harris, *J. Phys. Chem.*, **58**, 733 (1954).

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

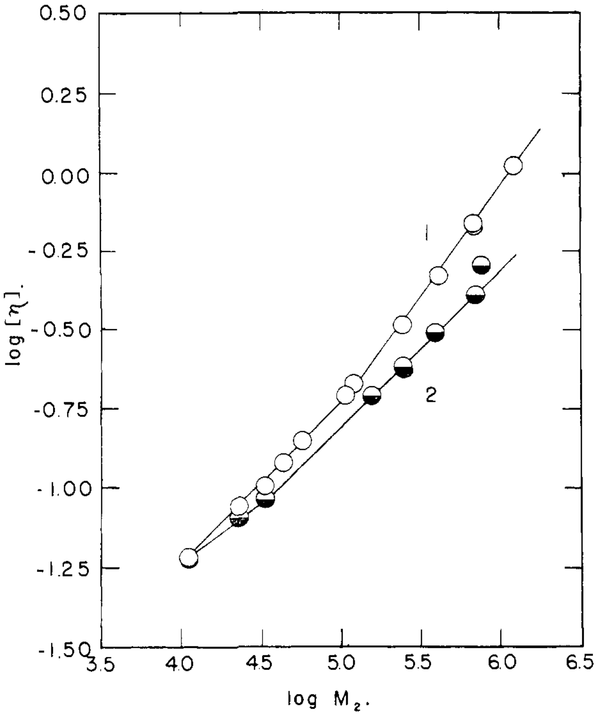

Fig. 1.—Log [η] *vs.* log M_2 for sodium polyphosphate in: (1) 0.35 *M* NaBr; (2) 0.415 *M* NaBr.

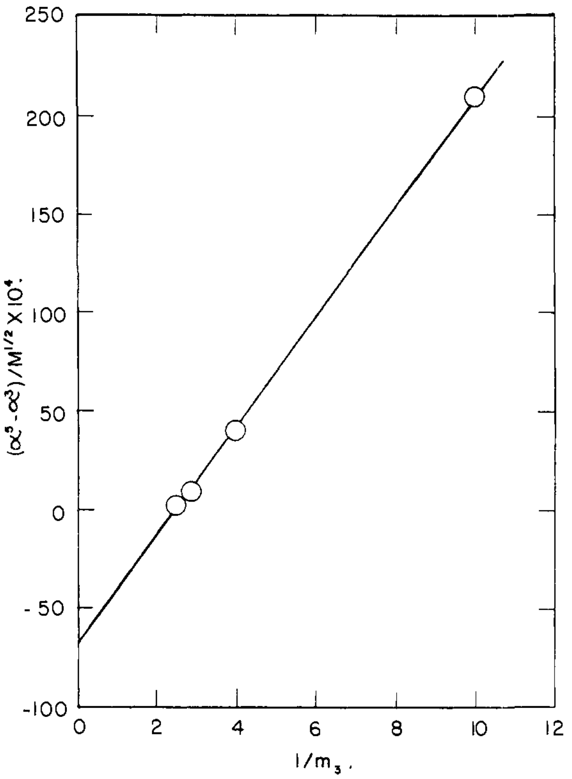

Fig. 2.—Dependence of the molecular expansion coefficient, α, of sodium polyphosphate (NaPP-7) on the sodium bromide molarity, m_3.

When theoretical expressions for β_{22} and β_{23} become available, equation 14 should become useful in relating molecular dimensions to charge and electrolyte concentration.[46]

In the meantime we may look upon equation 11 as an empirical equation which in form reproduces the experimental data. The intercept, *f*, which may be considered as a measure of the excluded volume of the hypothetical uncharged polymer, is equal to -6.9×10^{-3}.[47] This result confirms the solvent incompatibility of associated ($NaPO_3$) groups which has previously been hypothesized to account for differences in both intrinsic viscosity and salting-out behavior of polyphosphates in the presence of different alkali metal ions.[25]

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[46] The last term in equation 14 can be obtained rigorously from membrane equilibrium data, if β_{33} is known. From literature data (H. S. Harned and C. C. Crawford, THIS JOURNAL, **59**, 1903 (1937)), $(2 + \beta_{33}m_3)$ is found to be equal to 1.85 over the range investigated here. Then, with the membrane equilibrium data, the expression in braces in equation 14 simplifies to $\{[(i^2 - 0.025)/m_3] + (\beta_{22}/P^2)\}$ for our system. Using a realistic value for *i*, *e.g.*, one estimated from electrophoresis results, one finds that the term inside the brackets is an order of magnitude larger than the total experimental value of the expression inside the braces. Thus β_{22}/P^2 must be of opposite sign to the first term and also very large. Finally, to account for the slope of the line in Fig. 2 by equation 14, it is necessary that β_{22}/P^2 should have a large componenent which is inversely proportional to m_3.

[47] Such a large negative value so far has been reported only for neutralized polyacrylic acid in solutions of calcium salts (P. J. Flory and J. E. Osterheld, *J. Phys. Chem.*, **58**, 653 (1954)), but not for anionic polyelectrolytes in solutions of sodium salts where the intercept usually is close to zero. This also explains why the difficulty which we encountered in attempting to extrapolate the molecular dimensions to infinite ionic strength has not been observed in other polyelectrolyte-salt systems.

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The Spectrum and Structure of Disiloxane[1]

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The infrared absorption spectrum of disiloxane in argon and nitrogen matrices at 20°K. was investigated. The region covered was from 4000 to 600 cm.$^{-1}$. The band at 764 cm.$^{-1}$ in the gas phase is found to have two components in the matrix. The Raman band at 1009 cm.$^{-1}$ appears in the infrared spectrum of the matrix. A Si–O–Si bond angle of less than 180° is proposed to explain these results. The Si–O–Si bond angle is estimated to be near 155°.

It is now well established that the typical Si–O–Si bond angle is relatively large—near 160° rather than the range of 110° characteristic of many systems. The evidence includes the dipole moment measurements on methylsiloxanes by Sauer and Mead[3] and the crystal structure studies of crys-

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[2] National Science Foundation Fellow, 1954–1957.

[3] R. O. Sauer and D. J. Mead, THIS JOURNAL, **68**, 1794 (1946).