equal to the K value of the monomeric acid with one less unit of negative charge.

Throughout this paper, the formula of the dimeric chromium(VI) species which is predominant at pH 3 has been represented as $Cr_2O_7^=$. The data obtained in this study establish only the number of chromium(VI) atoms in the species (two) and the charge on the species (minus two). A representation as $(HCrO_4^-)_2$ would be equally good as far as these data are concerned. These two formulas $Cr_2O_7^=$ and $(HCrO_4^-)_2$ differ by one molecule of water and, as is often true, the determination of the extent of hydration of ionic species in aqueous solution can be very difficult. If the rate of exchange of O^{18} between solvent water and the oxygenated chromium(VI) species proves to be measurable, the results will be of value in connection with this question; such results have been of value in other such problems.[18]

[18] H. W. Crandall, *J. Chem. Phys.*, **17**, 602 (1949); J. P. Hunt and H. Taube, *ibid.*, **19**, 602 (1951).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

Polyphosphates as Polyelectrolytes. II. Viscosity of Aqueous Solutions of Graham's Salts[1]

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The viscosity behavior of aqueous solutions of several samples of sodium polyphosphate, covering a molecular weight range from 7000 to 19000, was investigated. The results for each sample could be represented by the Fuoss equation, $\eta_{sp}/C = A/(1 + B\sqrt{C}) + D$. The parameters A, B and D all increased with molecular weight. The intrinsic viscosity, $A + D$, was proportional to the 1.87th power of the molecular weight, indicating rod-like structure of the polyions at infinite dilution. The end-to-end distances of the polyions at infinite dilution, estimated from the intrinsic viscosity values, were of the same order of magnitude as their contour lengths, calculated from the molecular weights, confirming the absence of chain branching of these polyelectrolytes in solution.

In a previous paper, the viscosity and light scattering behavior of several samples of Graham salt in electrolyte solutions was reported.[2] The work was initiated for two reasons: first, in order to determine the molecular dimensions of these useful inorganic polyelectrolytes; second, in order to learn more about the behavior of polyelectrolytes. In the present paper a continuation of this study is presented, which deals with the viscosity behavior of the same Graham salt samples in pure water.

Experimental

The preparation of the eight samples of sodium polyphosphate, covering a molecular weight range from 7000 to 19,000, has been described.[2]

Viscosities were measured at 25° in the same Bingham viscometer and by the same procedure as was used previously.[2] Since the viscosities of the freshly prepared solutions decreased for about 12 hours after dissolution, all measurements reported in this paper were taken after this period, *i.e.*, when the viscosities had become constant. The soundness of this procedure has been established.[2] All viscosity results were found to be independent of the velocity gradient which was varied between about 2000 and 5000 sec.$^{-1}$.

Results and Discussion

The viscosity behavior of each sample was typical of flexible polyelectrolytes and could be accurately represented by the equation of Fuoss[3]

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

where C is the concentration in grams of solute per 100 ml. of solution, η_{sp}/C is the reduced viscosity, and A, B and D are constants characteristic of each sample. The data were fitted to this relation in the usual manner, by plotting $(\eta_{sp}/C - D)^{-1}$ against $C^{1/2}$, D being first approximately obtained from a plot of η_{sp}/C against $C^{-1/2}$ [4] and then adjusted to make the $(\eta_{sp}/C - D)^{-1}$ *vs.* $C^{1/2}$ curve perfectly linear. Three representative lines are shown in Fig. 1. From the intercepts, $1/A$, and the slopes, B/A, the constants A and B have been calculated. All the parameters of eq. 1 are collected in Table I. The molecular weights which are given in the second column for comparison were previously obtained by light scattering.[2,5]

TABLE I

FUOSS EQUATION PARAMETERS

Sample	M	D	$1/A$	B/A	A	B	$[\eta]$ in 0.35 N NaBr
134	7400	0.06	0.30	6.37	3.3	21	0.066
169	9800	.08	.20	4.57	5.0	23	
181	9900	.08	.13	4.17	7.7	32	
242	14000	.08	.10	2.77	10	28	.086
270	15800	.095	.06	2.40	17	40	
305	17100	.12	.06	2.11	17	35	
309	17400	.12	.05	2.07	20	41	
312	18200	.095	.06	2.00	17	33	.101

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[1] This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(30-1)1018. Most of the contents of this article formed part of a paper presented before the Division of Polymer Chemistry of the American Chemical Society, Atlantic City, New Jersey, September, 1952.

[2] U. P. Strauss, E. H. Smith and P. L. Wineman, THIS JOURNAL, **75**, 3935 (1953).

[3] R. M. Fuoss, *J. Polymer Sci.*, **3**, 603 (1948); correction, *ibid.* **4**, 96 (1949).

[4] W. N. Maclay and R. M. Fuoss, *ibid.*, **6**, 511 (1951).

[5] Incidentally, an empirical relationship between the viscosity of aqueous polyphosphate solutions and the molecular weight as determined by end-group titrations recently has been reported [R. Pfanstiel and R. K. Iler, THIS JOURNAL, **74**, 6059 (1952)]. Applying this relationship to our viscosity data, we find molecular weights about 60% of the light scattering values. This is of the right order of magnitude, considering the polydispersity of the samples and the different molecular weight averages measured by end-group titrations on the one hand (number-average) and by light scattering on the other (weight-average).

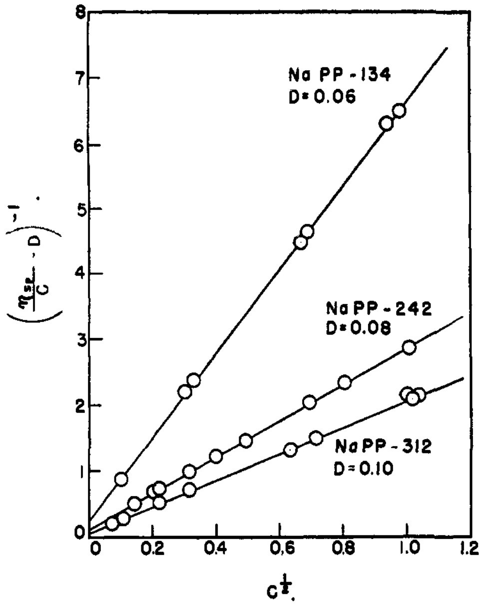

Fig. 1.—Test plots of Fuoss equation.

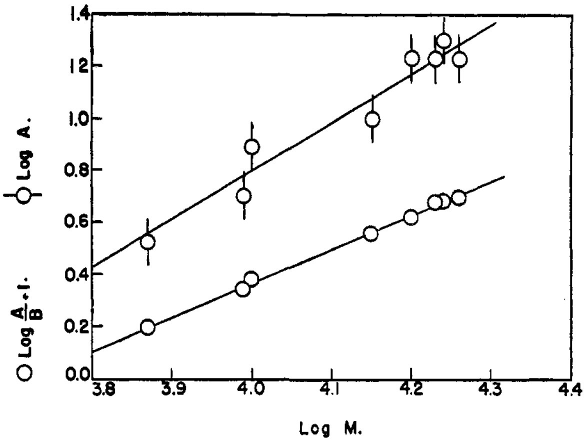

Fig. 2.—Dependence of Fuoss equation parameters on molecular weight.

Equation 1 shows that the intrinsic viscosity, *i.e.*, the limit of the reduced viscosity as the concentration approaches zero, is equal to $A + D$ which, since D is negligibly small, is for all practical purposes equal to A. Since the intercepts of the curves in Fig. 1 are too small to be determined very precisely, the values of A in Table I, which are derived from these intercepts, may deviate by as much as 15% from their true values. These possible deviations have been indicated by the vertical segments in the upper curve of Fig. 2 where the molecular weight dependence of A is shown on a log–log plot. The best straight line consistent with the precision of the experimental points has a slope of 1.87, a value close to the theoretical slope expected for stiff rod-like molecules.[6] This is an indication that the polyphosphate chains become highly extended as the ionic strength of the solution approaches zero, a conclusion which has also been reached by Van Wazer, Goldstein and Farber on the basis of flow birefringence measurements.[7]

The quantitative relationship between A and the molecular weight, obtained from the upper curve in Fig. 2, is given by the expression

$$A = 2.0 \times 10^{-7} \times M^{1.87} \qquad (2)$$

The parameter B in eq. 1 which determines the degree to which the reduced viscosity is affected by concentration changes has in two instances been reported to be independent of the degree of polymerization.[3,8] While the values of B in Table I are somewhat scattered,[9] they show a definite upward trend with increasing molecular weight. Even stronger evidence for the molecular weight dependence of B is contained in Fig. 2. If B were independent of the degree of polymerization, the upper and the lower curves whose ordinates represent log A and log $(A/B) + 1$, respectively, would be parallel, which they clearly are not. From the lower curve, one obtains the equation

$$A/B = 1.35 \times 10^{-6} \times M^{1.31} \qquad (3)$$

which combined with eq. 2 leads to the expression

$$B = 0.15 \times M^{0.56} \qquad (4)$$

The increase of B with the molecular weight is quite in line with our understanding of polyelectrolyte behavior While the polyions are highly extended at infinite dilution, they tend to coil up more and more as the concentration, and, with it the ionic strength, is increased. As a consequence, the power of M on which the reduced viscosity depends should decrease from about 2 at infinite dilution to about 1 when the concentration becomes very large. It is clear from eq. 1 that, at least in the lower concentration region where the term D is negligibly small, such a change in the molecular weight dependence of the reduced viscosity can come about only if B increases with molecular weight.[10]

The parameter D of eq. 1 also increases with molecular weight. By comparison with the last column in Table I, D is seen to be approximately equal to the intrinsic viscosity in 0.35 N sodium bromide solution. As has been shown before, this sodium bromide solution is an "ideal" solvent in which the net thermodynamic interactions between the polymer segments vanish, and the polyphosphate chains assume their intrinsic configurational character.[2,11] Such a correlation if it should prove to be a general property of polyelectrolytes, would furnish a reasonable physical interpretation for D, in line with some theoretical results reported by Katchalsky.[12]

In order to obtain some information concerning

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(6) J. G. Kirkwood and P. L. Auer, *J. Chem. Phys.*, **19**, 281 (1951).

(7) J. R. Van Wazer, M. Goldstein and E. Farber, THIS JOURNAL, **75**, 1563 (1953).

(8) A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

(9) This scattering is inherent in the fact that the parameter A, whose experimental indeterminacy is fairly large, is utilized in the calculation of B.

(10) If B were independent of the molecular weight, the reduced viscosity at any given finite concentration would be proportional to the same power of M as at infinite dilution. In the above discussion, the reduced viscosity is assumed to be determined mainly by the shape of the polyions. However, even if interactions between polyions were to make a significant contribution, it is highly improbable that they would exactly cancel the influence of the coiling effect considered above.

(11) P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

(12) A. Katchalsky, lecture given at Symposium on Polyelectrolytes, Polytechnic Institute of Brooklyn, September 29, 1951.

the molecular dimensions of the polyphosphate ions, it is of interest to estimate their end-to-end distance at infinite dilution from the intrinsic viscosity, A, and to compare this distance with their extended length.

The extended length, *i.e.*, the theoretical length of the chain if it were unbranched and completely extended, is obtained by multiplying the degree of polymerization, n, obtained from light scattering,[2] by 2.5 Å. which is the distance between two consecutive phosphorus atoms in the polymer chain.[7] Since $n = M/102$, one obtains the following equation for $\mathring{L}$, the extended length in ångström units

$$\mathring{L} = 0.025M \qquad (5)$$

Since L is to be compared with the viscosimetric end-to-end distance, R, a slight adjustment is necessary to allow for the fact that the samples are polydisperse and that L, being derived from the light scattering molecular weight, is a weight average value, while R corresponds to a somewhat higher average since it is derived from A which depends almost on the square of the molecular weight. The theory underlying this type of adjustment was developed by Flory.[13] Using eq. 6′ of ref. 13 with a for simplicity of calculation approximated by 2, one finds that the viscosity average molecular weight, M_v, is equal to the geometrical mean of the weight average and Z-average[14] molecular weights. The molecular weight distribution of the glassy polyphosphates has been given by Van Wazer.[15] Using eq. 3 of ref. 15, one finds that with this distribution which has also been verified experimentally,[16] $M_z = 1.5M_w$. Therefore $M_v = \sqrt{1.5} \times M_w$. The values of the extended length obtained from eq. 5 by the use of M_v, are given in the fourth column of Table II.

TABLE II

COMPARISON OF VISCOSIMETRIC END-TO-END DISTANCE WITH EXTENDED LENGTH

Sample	$M_w{}^a$	M_v	$\mathring{L}^b$	A^c (smoothed)	$\mathring{R}^d$	$\mathring{R}^e$	R^e/L
134	7400	9000	230	3.7	250	580	2.5
169	9800	12000	300	5.8	320	740	2.5
181	9900	12100	300	6.7	340	790	2.6
242	14000	17100	430	11.7	460	1110	2.6
270	15800	19300	480	14.5	510	1260	2.6
305	17100	20900	520	18.3	570	1370	2.6
309	17400	21200	530	18.9	580	1400	2.6
312	18200	22200	550	19.2	590	1430	2.6

[a] From light scattering.[2] [b] From eq. 5 using M_v. [c] From eq. 2. [d] From eq. 6 using M_v. [e] From Simha's equation.

To determine the end-to-end distance, R, from the intrinsic viscosity, A, several relations are at one's disposal. Among these, the following equation, derived by Flory and Fox[17] for flexible coils, has been verified experimentally up to an extension ratio, R/L, of 1/4[11,18,19]

$$R^3 = MA/(2.1 \times 10^{21}) \qquad (6)$$

The values of R, obtained by means of this relation, are shown in the sixth column of Table II. The apparent extension ratio, R/L, is seen to be near unity. In the case of nitrocellulose it has been shown that at such high extensions of the polymer chains, the use of eq. 6 leads to values of R which are too low.[19]

The following relation which has been derived by Simha[20] is suitable and has frequently been used for such high extension ratios[21,22]

$$A = \frac{v}{100}\left[\frac{f^2}{15(\ln 2f - 3/2)} + \frac{f^2}{5(\ln 2f - 1/2)} + \frac{14}{15}\right] \qquad (7)$$

where f is the ratio of the length and diameter of the ellipsoid of revolution which serves as a model for the extended polymer molecule, and v is the effective specific volume of the ellipsoid, here approximated by 0.39, the partial specific volume of sodium polyphosphate as reported by Malmgren.[23] The values of f, obtained from eq. 7, are converted to values of R with the help of an additional relation in which the volume of the molecule, as calculated from the molecular weight and partial specific volume, is equated with the formula for the volume of the equivalent ellipsoid. The results which, incidentally, are quite insensitive to the value of v used in the above calculation are given in the seventh column of Table II.

The fact that R is somewhat larger than L may be due to the approximate nature of both eq. 7 and the model of the polymer molecule employed. It may also be that the contribution of intermolecular forces to the reduced viscosity at finite concentrations does not completely disappear on extrapolation to infinite dilution by eq. 1.

However, since R and L are of the same order of magnitude and since their ratio which is shown in the last column of Table II is constant over the whole molecular weight range investigated, it seems reasonable to conclude that the intrinsic viscosity is essentially governed by the extended length of the polyions according to Simha's equation. Since the extended length was calculated assuming the absence of branching, these results confirm the conclusion reached by Van Wazer on the basis of titration experiments that the polyphosphate ions exist as linear, unbranched chains in solution.[24]

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(13) P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

(14) W. D. Lansing and E. O. Kraemer, *ibid.*, **57**, 1369 (1935).

(15) J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

(16) J. R. Van Wazer, *ibid.*, **72**, 647 (1950).

(17) P. J. Flory and T. G. Fox, *J. Polymer Sci.*, **5**, 745 (1950).

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

(19) S. Newman and P. J. Flory, *J. Polymer Sci.*, **10**, 121 (1953).

(20) R. Simha, *J. Phys. Chem.*, **44**, 25 (1940).

(21) C. W. Tait, R. J. Vetter, J. M. Swanson and P. Debye, *J. Polymer Sci.*, **7**, 261 (1951).

(22) D. T. F. Pals and J. J. Hermans, *Rec. trav. chim.*, **71**, 433 (1952).

(23) H. Malmgren, *Acta Chem. Scand.*, **2**, 147 (1948).

(24) J. R. Van Wazer, THIS JOURNAL, **72**, 639 (1950).