Stadler is applicable the exchange half-time should have been very considerably less than 28,000 hours (we calculate 28,000 hours for 25°). Actually no measurable exchange was observed in any of five samples taken over a period of 1600 hr. From the estimated limits of counting error the exchange half-time was $> 5 \times 10^5$ hr. For exchange through the sixth order path we estimate that the half-time would be of the order of 10^{10} hours for these conditions. The observed fifth order law may possibly be related to the sixth order law with $X^- = I^-$.

The Exchange Mechanism.—We may speculate upon the reaction mechanism responsible for this sixth order rate law. A plausible one involves these rapid, reversible equilibria (where we represent associated ion pairs as A^+B^-)

$$\begin{gathered} H^+ + IO_3^- = HIO_3 \\ HIO_3 + H^+ = IO_2^+ + H_2O \\ IO_2^+ + X^- = IO_2^+X^- \\ H^+ + I^- = H^+I^- \end{gathered}$$

The possible formation of the ion IO_2^+ was suggested to us by the behavior of nitric acid, which has recently been shown[18,19] to form a reactive ion NO_2^+ especially in the presence of perchloric or sulfuric or other very strong acid. (It may be noted that iodic acid like nitric acid forms a double compound with concentrated perchloric or sulfuric acid.) The rate determining step might then be a two-electron transfer between the iodine species in the two ion pairs

$$IO_2^+X^- + H^+I^- = (H^+, I^-, IO_2^+, X^-) \longrightarrow HIO_2 + I^+X^-$$

It is presumed that these products would react rapidly with hydriodic acid to give iodine and water[20] (and X^- ion).

For experiments in which the apparent iodate dependence is 1.8 (*i. e.*, $X^- = IO_3^-$) it is seen that two iodate ions must enter the transition state in some form. If one were not reduced (as suggested in the above mechanism) and, further, if it became equivalent at any stage to an iodine atom originally present as iodide, then the addition of labelled (radioactive) hydriodic acid to an excess of iodic acid should result immediately in labelled iodic acid. We carried out such experiments under a variety of conditions, and no activity was detected in the residual iodic acid; this shows that the pentavalent iodine retains its identity, if indeed the transition state does split off iodate ion in this case.

Summary

The experimentally observed rate law for the iodine–iodate exchange reaction has been determined to be $R = (I_2)^{0.6}(H^+)^{1.8}(IO_3^-)^{0.8}[k(IO_3^-) + k'(X^-)]\Gamma$, in which X^- may be perchlorate, nitrate or sulfate ion, and Γ indicates that the activity coefficients of reactants and transition states are to be introduced with the appropriate powers. At 25° k has the value (7.40 ± 0.25) $l.^{3.2}$ mole$^{-3.2}$ hr.$^{-1}$ and k' is roughly 0.15 $l.^{3.2}$ mole$^{-3.2}$ hr.$^{-1}$ for $X^- = ClO_4^-$. The activation energy is approximately 20 kcal. mole^{-1}.

The exchange mechanism is shown to be the reversible reaction between iodide and iodate ions at equilibrium. Therefore the rate law for that reaction at very low iodide concentration is $-d(IO_3^-)/dt = (I^-)(IO_3^-)(H^+)^3[k_6(IO_3^-) + k_6'(X^-)]\Gamma$, in which k_6 at 25° is $(5.7 \pm 1.3) \times 10^6$ $l.^5$ mole^{-5} sec.$^{-1}$ and k_6' for $X^- = ClO_4^-$ is *ca.* 1.1×10^5 $l.^5$ mole^{-5} sec.$^{-1}$ at 25°.

A possible reaction mechanism is proposed which involves as a rate determining step a two-electron transfer from a chemical species containing I^- to one containing IO_2^+.

ST. LOUIS, MISSOURI RECEIVED MAY 31, 1949

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[18] Hughes, Ingold and Reed, *Nature*, **158**, 448 (1946).

[19] Ingold and co-workers, *ibid.*, **158**, 480 (1946).

[20] Bray, THIS JOURNAL, **52**, 3580 (1930).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE RUMFORD DIVISION OF HEYDEN CHEMICAL CORPORATION]

Structure and Properties of the Condensed Phosphates. V. Molecular Weights of the Polyphosphates from Viscosity Data

BY JOHN R. VAN WAZER*

According to the theory and data presented in the first three papers of this series,[1] sodium phosphate glasses in the composition range between $Na_2O \cdot P_2O_5$ and $2Na_2O \cdot P_2O_5$ consist of polyphosphates, the average molecular weight of which becomes very large as the Na_2O/P_2O_5 ratio approaches unity. Since intrinsic viscosity is a function of molecular weight, viscosity measurements in solutions which are concentrated with respect to a simple salt (in order to minimize the effect of the ionic charge of the phosphate) and dilute with respect to the phosphate, should serve as an additional independent check of the polyphosphate theory of structure. If this theory presents a reasonable picture of the situation, such viscosity measurements should be related to the molecular weights, obtained from end-group titrations, by the equation[2] which was developed to fit data on organic high polymers and should result in reasonable values for the characteristic constants in this equation.

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[1] Van Wazer, THIS JOURNAL, **72**, 639, 644, 647 (1950).

[2] *E. g.*, Baker, Ford and Heiss, *ibid.*, **63**, 3316 (1941).

Preliminary Theory.—A number of investigators[2] have shown that the intrinsic viscosity,[3] $[\eta]$, is related to the viscosity average molecular weight,[4] $\bar{M}_v$, in the domain of molecular weights below *ca.* 6000 by an equation which contains two characteristic constants, K_i and K_0

$$[\eta] = K_i \bar{M}_v + K_0 \qquad (1)$$

End-group titrations give number average molecular weights, which are almost certain to be approximately proportional to the viscosity average molecular weights for any type of distribution. For the logarithmic distribution corresponding to random reorganization, the weight average is nearly equal to twice[5] the number average in the region of number average chain lengths greater than *ca.* 8.

In this series of papers, we have found it convenient to report the data in terms of the average number of phosphorus atoms per polyphosphate chain, *i. e.*, the polyphosphate chain length, rather than in terms of molecular weights, since we are primarily interested in the polyphosphate anions, the "molecular weights" of which will be dependent on their accompanying cations. Of course, the ionic weight of polyphosphate anions having one associated hydrogen atom at each end is related to the number of phosphorus atoms per polyphosphate chain, n, by the equation

$$M = 79.0\,n + 18 \qquad (2)$$

Experimental

An Ostwald-type capillary tube viscosimeter constructed according to the design of Fenske and Cannon[6] to eliminate drainage and tilting errors, was used in the viscosity measurements. Since the viscosimeter had a flow time of about 300 sec. with pure water, no kinetic energy corrections were necessary and the kinematic viscosity could be obtained directly from the time of flow. During a measurement the viscosimeter was kept in a thermostat to maintain the temperature at 25.0°.

The densities of the solutions were obtained with a Westphal balance. To obtain the greatest precision a large scale plot of measured density *vs.* concentration was made for each concentration series, and the values of the densities used to convert kinematic to absolute viscosities were taken from a smooth curve drawn through the measured points.

In most of the experiments a 10% solution of tetramethylammonium bromide was used as solvent and a supply of several liters of this solution was made up when the problem was started. The vitreous sodium phosphates were dissolved directly in the tetramethylammonium bromide solution. No attempt was made to prepare the tetramethylammonium salts of the phosphates, since it was assumed that as the phosphate concentration was reduced, the increasing large ratio of tetramethylammonium to sodium ion would prevent any complication due to complex formation between the sodium and polyphosphate when the intrinsic viscosity was measured. Each measurement was carried out as follows: The viscosity of the pure tetramethylammonium bromide solution was determined and this was followed by three successive determinations of the viscosity of a freshly prepared solution containing the phosphate. Usually this complete series of determinations was repeated. Except for the glass having the highest number average molecular weight, there seemed to be no systematic change in the viscosity due to hydrolysis during a measurement. In the case of this glass, for which $\bar{n}_N = 289$, the viscosity data were extrapolated back to the time at which the finely powdered glass was added to the tetramethylammonium bromide solution. By this means the effect of hydrolysis was overcome. It should be noted that the correction to the measured viscosity introduced by this extrapolation was less than 0.5% at all concentrations. Although the *p*H was not adjusted in these determinations, it always lay between 7 and 9.

The viscosity measurements were carried out at four different concentrations for each phosphate glass studied. The intrinsic viscosity was obtained from a plot of log relative viscosity *vs.* concentration (g. glass/100 ml. solution). In the case of the glasses for which $\bar{n}_N$ was greater than *ca.* 10, the two points corresponding to the lower concentrations were found to lie in a straight line with the origin.

Preparation of the sodium phosphate glasses and determination of their number-average chain lengths (with small corrections for the presence of water of constitution, metaphosphate rings and orthophosphates) were carried out as described in paper III.

Results and Discussion

When the sodium phosphate glasses were dissolved in pure water, it was found that the ratio of the specific viscosity to concentration increased without limit as the concentration decreased. This is in accord with the findings of those[7,8] who have previously worked with ionized polymers. When the sodium phosphate glasses were dissolved in the 10% solution of tetramethylammonium bromide, it was seen that the viscosity varied in the same manner as has been found for un-ionized polymers. This result also agrees with the previous work.

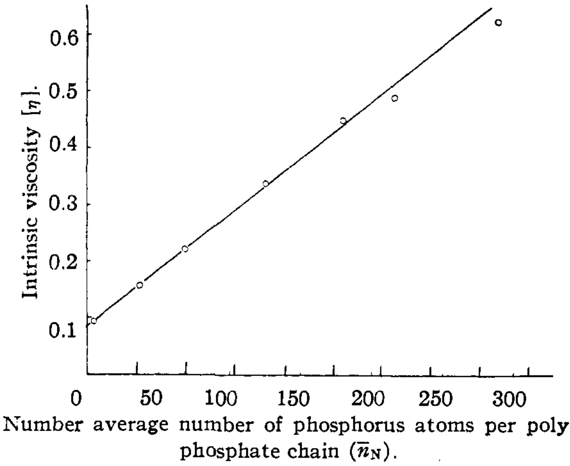

Fig. 1.—Variation of intrinsic viscosity with polyphosphate chain length computed from *p*H titration data.

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(3) Defined by Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).

(4) The viscosity average defined by Flory, THIS JOURNAL, **65**, 372 (1943), reduces to a weight average for the case under consideration.

(5) Bawn, "Chemistry of High Polymers," Interscience Publishers, Inc., New York, N. Y., 1948, p. 35.

(6) Fenske and Cannon, *Ind. Eng. Chem., Anal. Ed.*, **10**, 297 (1938).

(7) Staudinger, "Die hochmolekularen organischen Verbindungen," Springer, Berlin, 1932, Part IID by Staudinger and Trommsdorf.

(8) Fuoss and Strauss, *J. Polymer Sci.*, **3**, 246 (1948); **3**, 602 (1948).

TABLE I

SPECIFIC VISCOSITY OF SODIUM PHOSPHATE GLASSES AS MEASURED IN 10% TETRAMETHYLAMMONIUM BROMIDE SOLUTION AT 25°

% of P_2O_5, grav.	% of H_2O, pH titrn.	No. av. ch. length by end-group titrn.	% total P in meta rings (Fig. 4 of III)	Viscosity data: Glass in soln., g./100 ml.	Soln. density	Spec. visc.
61.7	0.08	4.66	0.0	2.00	1.0380	0.0952
				1.00	1.0316	.0583
				0.50	1.0284	.0380
				0.25	1.0266	.0226
				0	1.0249	.000
					$[\eta] = 0.090$	
68.7	.10	37.0	4.8	1.50	1.0347	.132
				0.75	1.0300	.0940
				.375	1.0277	.0558
				.188	1.0262	.0295
				0	1.0249	.000
					$[\eta] = 0.157$	
69.0	.02	68.5	5.7	1.00	1.0315	.180
				0.50	1.0283	.1056
				.25	1.0267	.0552
				.10	1.0256	.0223
				0	1.0249	.000
					$[\eta] = 0.216$	
69.3	.05	125	5.9	1.00	1.0315	.288
				0.50	1.0282	.170
				.25	1.0266	.0870
				.10	1.0256	.0350
				0	1.0249	.000
					$[\eta] = 0.338$	
69.4	.04	180	6.1	0.450	1.0279	.190
				.300	1.0269	.134
				.150	1.0260	.0696
				.100	1.0256	.0455
				0	1.0249	.000
					$[\eta] = 0.453$	
69.4	.02	216	6.1	0.500	1.0282	.243
				.250	1.0266	.129
				.125	1.0258	.0632
				.063	1.0254	.0318
				0	1.0249	.000
					$[\eta] = 0.486$	
69.6	.01	289	6.6	0.300	1.0269	.190
				.200	1.0263	.130
				.100	1.0256	.0651
				.050	1.0253	.0318
				0	1.0249	.000
					$[\eta] = 0.622$	

A plot of intrinsic viscosity *vs.* average chain length is presented in Fig. 1. From this plot it is seen that the constants of equation 1 have the following values, based on the assumption that the weight average is twice the number average

$$K_0 = 0.085$$

$$K_i = [\eta] - K_0/(79\bar{n}_w + 18) = 1.25 \times 10^{-5}$$

These values are quite in line with the published data on *n*-paraffins in the carbon tetrachloride,[9] polyoxyethylene glycol in carbon tetrachloride,[10] and polydecamethylene glycol adipate in diethyl succinate or in chlorobenzene.[11]

Several recent Swedish papers[12,13] have presented viscosity data on polymeric phosphates. The paper[13] by Malmgren is especially interesting in that it gives a relationship between $(\eta_{sp}/C)_{c\to 0}$ and ionic strength for a potassium polymetaphosphate having an average molecular weight[5] of 1.3×10^6 as measured in an ultracentrifuge. In paper I it was demonstrated that all phosphate anions in aqueous solution must be either unbranched chains or rings. Therefore, Malmgren's potassium metaphosphate is undoubtedly a polyphosphate (straight chain anion), since very large rings are not only improbably difficult to form but also are converted to polyphosphates when the first P–O–P linkage per ring is broken in hydrolysis. Since a 10% tetramethylammonium bromide solution has an ionic strength, μ, equal to 0.33, Malmgren's value of $(\eta_{sp}/C)_{c\to 0}$ = *ca.* 30 for μ = 0.33 in sodium thiocyanate should lead to an approximate value for the molecular weight when substituted in equation (1) with the constants given herein, assuming, of course, that $(\eta_{sp}/C)_{c\to 0} = [\eta]$. When this is done, $\bar{M}_w$ is found to equal 3.5×10^6, based on the $(KPO_3)_n$ formulation. This value has the right order of magnitude but is probably several times too large to be exactly in accord with the ultracentrifuge value. In view of the large mathematical extrapolation involved and the fact that Malmgren used sodium thiocyanate and we used trimethylammonium bromide as the added salt, some difference between the values is to be expected. The observed accordance can be interpreted as additional confirmation of the over-all ideas advanced in this series of papers.

Acknowledgment.—I would like to thank Mrs. Doris Campanella for carrying out most of the measurements reported in this paper.

Summary

Viscosities were measured on dilute solutions of sodium phosphate glasses in water containing 10% tetramethylammonium bromide, and it was found that the intrinsic viscosity was linearly related to the average number of phosphorus atoms per polyphosphate chain.

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[9] Meyer and van der Wijk, *Helv. Chim. Acta*, **18**, 1067 (1935).

[10] Fordyce and Hibbert, THIS JOURNAL, **61**, 1912 (1939).

[11] Flory and Stickney, *ibid.*, **62**, 3032 (1940).

[12] Drucker, *Acta Chem. Scand.*, **1**, 221 (1947); Ingelman and Malmgren, *ibid.*, **1**, 422 (1947).

[13] Malmgren, *ibid.*, **2**, 147 (1948).