Viscometric Studies of Solutions of Sodium Phosphates, Graham Salts and Vanadium-containing Graham Salts

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Graham salt (amorphous sodium polyphosphate) has often been interested in by many investigators recently[1,2], and it has been made clear that the substance has typical features as a linear-chain polyelectrolyte in a solution. However, the polymer molecules are sometimes decomposed in the solution, especially when the polymer is branched. The points of branching are belived to capable of being hydrolyzed readily.

In the present paper, the degradation of polyphosphate is studied by viscometry. For the sake of the study, it was necessary to know the relation between the intrinsic viscosity and the molecular weight, especially for low molecular weight polyphosphates. Furthermore, vanadium-containing Graham salt (sodium vanadate-phosphate copolymer) was studied, because the –V–O–P– chain was expected to be hydrolyzed much easier than the –P–O–P– chain. Ohashi and Matsumura[3] previously obtained some information on the structures of the glasses and crystals of sodium vanadate-phosphates from paper chromatographic analysis of their solutions.

Experimental

Sodium Phosphates.—Commercial specimens of a guaranteed reagent grade of sodium dihydrogen orthophosphate ($NaH_2PO_4\cdot 2H_2O$), disodium hydrogen orthophosphate ($Na_2HPO_4\cdot 12H_2O$), sodium orthophosphate ($Na_3PO_4\cdot 12H_2O$) and sodium pyrophosphate ($Na_4P_2O_7\cdot 10H_2O$) were used without further purification. Sodium tripolyphosphate ($Na_5P_3O_{10}\cdot 6H_2O$) of an extra pure reagent grade was recrystallized four times from an alcohol-water mixture. In order to check the purity and the amount of crystallization water, the content of each phosphate was measured by potentiometric titration, using 0.1 N sodium hydroxide for sodium dihydrogen orthophosphate and using 0.1 N hydrochloric acid for the other four phosphates. All results agreed well with the theoretical values within the range of experimental error.

Graham Salts. — Amorphous sodium polyphosphates (Graham salts) of various degrees of polymerization were prepared[4] by heating under the conditions described in Table I; they were then quenched by being pressed between two sheets of copper plate. The degrees of polymerization, $\bar{n}$, as determined by pH-titration[5], are also cited in Table I.

TABLE I. PREPARATION OF GRAHAM SALTS

Sample	Starting material, g.	Heating	$\bar{n}$
A	$NaPO_3$ 29.6 $Na_4P_2O_7$ 25.8	900°C, 1 hr.	4.4
B	$NaPO_3$ 40.3 $Na_4P_2O_7$ 13.5	900°C, 1 hr.	8.6
C	$NaPO_3$ only	900°C, 1 hr.	92
D	$NaPO_3$ only	alternately at 500 and 700°C, 1 week	100
E	$NaPO_3$ 48.1 $Na_4P_2O_7$ 2.6	900°C, 1 hr.	29

Vanadium-containing Graham Salts.—Calculated amounts of Graham salt ($NaPO_3$), vanadium pentoxide (V_2O_5) and sodium carbonate (Na_2CO_3) were mixed and heated at 900°C for 1 hr. and were then quenched by being pressed with copper plates. It was recognized that a part of the vanadium was reduced to V^{4+} during the heating. The amount of V^{4+} was determined by the volumetric method[3]. The per cent of V^{4+} in the total vanadium is given in Table II.

TABLE II. SODIUM VANADATE-PHOSPHATE COPOLYMERS

Sample	Mole ratio P/V	V^{4+}, %	$\bar{n}'$	$\bar{n}$
F	100	40.0	167.7	83.35
G	50	39.4	85.6	42.30
H	10	33.7	21.1	7.62
I	7	30.0	17.1	5.96
J	4	22.9	13.9	3.66
K	1	4.6	28.3	0.98

If it is assumed that all the V^{4+} exists in the solution as gegen ions in the form of VO^{2+}, the average number of residues (both phosphate and

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[1] J. R. Van Wazer, "Phosphorus and its Compounds", Vol. I, Interscience Publishers, New York (1958).

[2] C. F. Callis, J. R. Van Wazer and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954).

[3] S. Ohashi and T. Matsumura, This Bulletin, **35**, 501 (1962).

[4] Prepared by one of the authors (S. O.) at the Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa.

[5] J. R. Van Wazer, E. J. Griffith and J. F. McCullough, *Anal. Chem.*, **26**, 1755 (1954); E. J. Griffith, ibid., **28**, 525 (1956).

vanadate residues) in one molecule, $\bar{n}'$, may be calculated by the equation:

$$\frac{\bar{n}'+2}{\bar{n}'}=\frac{\mathrm{Na}+2\mathrm{V}^{4+}}{\mathrm{P}+\mathrm{V}^{5+}} \qquad (1)$$

where Na, P, V^{4+}, and V^{5+} indicate the atomic ratio of these atoms. The value of $\bar{n}'$ is given in Table II. As will be described in a later section, the value of $\bar{n}'$ is too large to explain the intrinsic viscosity. Therefore, it was further assumed that the molecular chain in the solution was cut off at both sides of V^{5+}, probably due to hydrolysis, remaining as the polymer chains containing PO_3^- only and that no V^{5+} atom had been at the end of the original chain. The degree of polymerization, $\bar{n}$, of the remaining phosphate chains could then be calculated by dividing the $\bar{n}'$ value into the number of P atoms (P) and V atoms (V), and by using the following equation:

$$\bar{n}=\frac{(\mathrm{P})}{(\mathrm{V})+1} \qquad (2)$$

The value of $\bar{n}$ is also given in Table II.

Preparation of Solutions.—Samples of a known weight were dissolved in an aqueous 0.035 N or 0.07 N solution of sodium bromide at room temperature and were made up to the required volume. Orthophosphates, pyrophosphate, and tripolyphosphate dissolved immediately in the solvent (a sodium bromide solution). The concentration, c (g./100 ml.), of the solution was expressed as that of anhydride. The Graham salt used was in the form of small transparent pieces about 1～2 mm. thick which took time to dissolve when the molecular weight was high. It was, however, dissolved within 30～40 min. under agitation by a magnetic stirrer. Since Graham salt containing vanadium took a long time to dissolve, it was pulverized by using a mortar of agate and dried over $\mathrm{P}_2\mathrm{O}_5$ under reduced pressure. This pulverized sample still took about 0.5～1 hr. to dissolve, however.

Viscometry.—The viscosity of the solutions were measured by Ostwald's viscometer in a thermostat at 25.5°C. The correction term for kinetic energy was determined by using water and ethanol, but the value was so small that it was disregarded in further calculations.

The viscosities of solutions of samples **C** and **D** changed for 5～6 hr. after the beginning of dissolution. Thereafter, the viscosities were constant and did not change for more than 24 hr. No change of viscosity with time was observed for the other samples.

Density.—The density of the solutions was measured at 25.5°C by using Ostwald's pycnometer, whose content was about 5～6 ml. The density of solutions was linear to the polymer concentration, so that the density increment, $\varDelta$, was calculated by the equation:

$$\varDelta=100\left(\frac{d}{d_1}-1\right)\Big/c \qquad (3)$$

where d and d_1 are the densities of solution and solvent respectively, and where c is the concentration in g./100 ml.

Results and Discussion

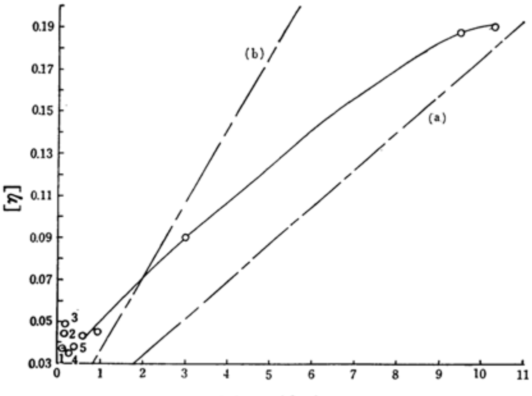
The Intrinsic Viscosities and Molecular Weight of Sodium Phosphates and Graham Salts.—The intrinsic viscosities $[\eta]$ of low molecular weight sodium phosphates and of Graham salts which do not contain vanadium were calculated by extrapolating both η_{sp}/c and $\ln \eta_r/c$ to infinite dilution on the basis of viscosity values measured at the polymer concentrations of 0.1, 0.2, 0.4, 0.8, 1.2 1.6 and 2.0 (g./100 ml). For these calculations, the viscosity values divided by the viscosity of solvent was used as the relative viscosity. Since the Graham salt is a kind of polyelectrolyte, its reduced viscosity (η_{sp}/c) should increase steeply when the polymer concentration is decreased if the concentration of the swamping electrolyte is not sufficiently high. This effect was observed in the case of 0.035 N sodium bromide, so that the intrinsic viscosity was obtained by neglecting the data at low polymer concentrations. In the case of 0.07 N sodium bromide, the effect was not observed and the extrapolation was easy, although in some instances abnormal values were obtained at very low concentrations. The results obtained in a 0.035 N sodium bromide

TABLE III. INTRINSIC VISCOSITY AND DENSITY INCREMENT OF SODIUM PHOSPHATE SOLUTIONS IN 0.035 N NaBr AT 25.5°C

Sample	$\bar{n}$	$[\eta]$	$\varDelta$
$\mathrm{NaH_2PO_4}$	1	0.037	0.706
$\mathrm{Na_2HPO_4}$	1	0.044	0.914
$\mathrm{Na_3PO_4}$	1	0.049	1.048
$\mathrm{Na_4P_2O_7}$	2	0.035	0.842
$\mathrm{Na_5P_3O_{10}}$	3	0.038	0.851
A	4.4	0.043	0.818
B	8.6	0.045	0.819
E	29	0.090	0.788
C	92	0.188	0.812
D	100	0.191	0.782

TABLE IV. INTRINSIC VISCOSITY AND DENSITY INCREMENT OF SODIUM PHOSPHATE SOLUTIONS IN 0.07 N NaBr AT 25.5°C

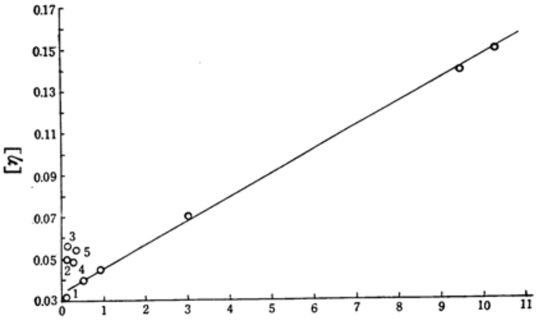
Sample	$\bar{n}$	$[\eta]$	$\varDelta$
$\mathrm{NaH_2PO_4}$	1	0.0313	0.609
$\mathrm{Na_2HPO_4}$	1	0.0500	0.758
$\mathrm{Na_3PO_4}$	1	0.0561	0.936
$\mathrm{Na_4P_2O_7}$	2	0.0486	0.767
$\mathrm{Na_5P_3O_{10}}$	3	0.0544	0.725
A	4.4	0.040	0.818
B	8.6	0.045	0.784
E	29	0.070	0.722
C	92	0.139	0.701
D	100	0.149	0.713



M, $\times 10^{-3}$

Fig. 1. Relation between $[\eta]$ and M in the solution of 0.035 N NaBr.

1 NaH_2PO_4	2 Na_2HPO_4
3 Na_3PO_4	4 $Na_4P_2O_7$
5 $Na_5P_3O_{10}$	



M, $\times 10^{-3}$

Fig. 2. Relation between $[\eta]$ and M in the solution of 0.07 N NaBr.

1 NaH_2PO_4	2 Na_2HPO_4
3 Na_3PO_4	4 $Na_4P_2O_7$
5 $Na_5P_3O_{10}$	

solution and in a 0.07 N sodium bromide solution are given in Table III and Table IV respectively. The value of $[\eta]$ is that for 20～24 hr. after the dissolution, if any time dependency of the viscosity (in the case of sample C and D) was observed. The $[\eta]$ values thus obtained are shown in Fig. 1 and Fig. 2 against the average molecular weight, M, the molecular weight of Graham salts was calculated by:

$$M = (Na_2O) + (NaPO_3) \times \bar{n} \tag{4}$$

Here (Na_2O) and $(NaPO_3)$ indicate their formula weights.

The intrinsic viscosity of Graham salt in a 0.035 N sodium bromide solution had already been measured by Strauss et al.[6], who summarized their results in an empirical equation:

$$[\eta] = 1.76 \times 10^{-5} \times M_w \tag{5}$$

In this equation, the weight average molecular weight, M_w, was used. It has been stated by Van Wazer[7] that the molecular weight of Graham salt shows a Poisson distribution and that the weight average molecular weight is just twice the number average molecular weight, M_n. Therefore, Eq. 5 may be rewritten as:

$$[\eta] = 3.52 \times 10^{-5} \times M_n \tag{6}$$

In Fig. 1, Eqs. 5 and 6 are shown by the straight lines a and b respectively. For the experimental data of Fig. 1, the molecular weight, M, was calculated by Eq. 4, on the basis of $\bar{n}$ values obtained by the determination of the end groups. The experimental molecular weight is, therefore, the number average molecular weight. The experimental data in Fig. 1 are located between the straight lines a and b. This would mean either that the distribution of the molecular weight is not exactly the Poisson distribution, or that the Eq. 5 derived originally for $M_w = 7000 \sim 19000$ has been extrapolated unreasonably to too low a molecular weight.

When 0.035 N sodium bromide is used as the solvent, the experimental values (Fig. 1) showed a linear relationship if $\log[\eta]$ was drawn against $\log M$ at the range of $M = 930 \sim 10300$; the following equation was obtained.

$$[\eta] = 6.9 \times 10^{-4} \times M^{0.61} \tag{7}$$

When 0.07 N sodium bromide was used as the solvent, the experimental data of $[\eta]$ were linear against M, as is shown in Fig. 2. The relation can be expressed for $M = 510 \sim 10300$,

$$[\eta] = 0.0348 + 0.112 \times 10^{-4} \times M \tag{8}$$

The intrinsic viscosity of sodium phosphates of low molecular weight shows a complicated dependency upon the molecular weight, dependent both on the shape of the molecule and on the degree of hydration. The latter is the greater, the greater the value of the density increment, Δ, because the following equation can be derived readily.

$$\Delta = \Delta V + 1/d_1 - 1/d_2 \tag{9}$$

Here, ΔV (ml./g.) is the volume contraction per 1 g. of solute, and d_1 and d_2 are the densities of the solvent and solute respectively. The value of d_1 is about 1.00 and that of d_2 is pressumed to be about 2.0～2.5, so that the value of the density increment should be equal to 0.5～0.6, if there is no volume contraction, while it should be greater than that value if there is any volume contraction. It

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[6] U. P. Strauss, E. H. Smith and P. L. Wineman, *J. Am. Chem. Soc.*, **75**, 3935 (1953).

[7] J. R. Van Wazer, ibid., **72**, 644, 647 (1950).

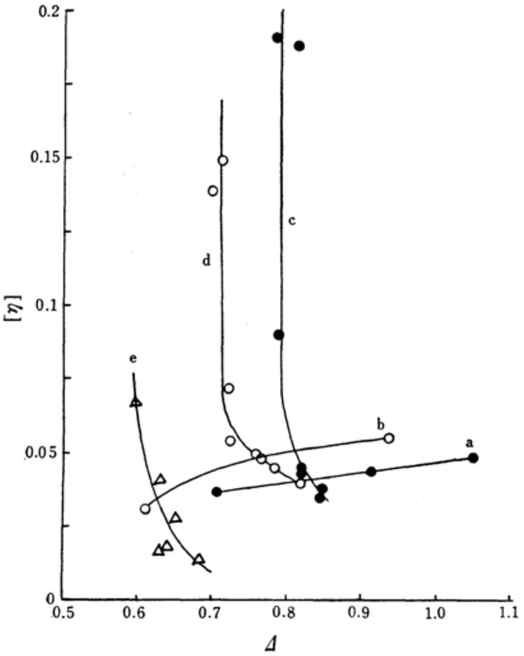

Fig. 3. Relation between [η] and Δ of sodium polyphosphate not containing vanadium in 0.035 N NaBr (●) and in 0.07 N NaBr (○), and containing vanadium in 0.07 N NaBr (△).

has been widely accepted that the hydration of ions results in volume contraction.

The relation between the density increment and the intrinsic viscosity is shown in Fig. 3. For the mono-, di- and tri-sodium orthophosphates, the density increment increases in the sequence and the intrinsic viscosity increses according to the increase in the degree of hydration, as is shown by curves a and b. However, the concentration of the swamping electrolyte is the higher, the smaller the degree of hydration, probably because of the dehydrating action of the swamping electrolyte. The value of the intrinstic viscosity, however, does not decrease in accord with the decrease in the density increment, so that the experimental data falls in the different curves a and b in Fig. 3. (Also, compare c and d.)

In the case of the polyphosphates, including pyro- and tripoly-phosphates, the relation between the density increment and the intrinsic viscosity is entirely different from the case with orthophosphates, the data fall on curves c and d. In this case, the shape of the molecule or the value of $\bar{n}$ seems to be more important than the degree of hydration, as has already been described.

TABLE V. INTRINSIC VISCOSITY AND DENSITY INCREMENT OF VANADIUM-CONTAINING GRAHAM SALTS IN 0.07 N NaBr SOLUTION AT 25.5°C

Sample	$\bar{n}$	[η]	Δ
F	83.35	0.0671	0.597
G	42.30	0.0407	0.631
H	7.62	0.0225	0.630
I	5.96	0.0232	0.641
J	3.66	0.0275	0.653
K	0.98	0.0135	0.683

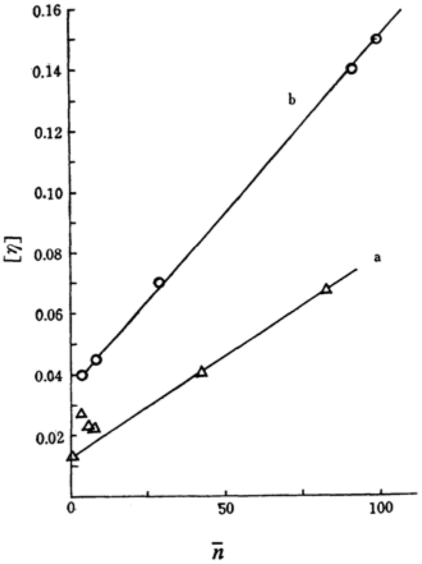

Fig. 4. Relation between [η] and $\bar{n}$ of vanadium containing (△) and not containing (○) Graham salt in 0.07 N NaBr.

The Intrinsic Viscosity of Vanadium Containing Graham Salts.—The intrinsic viscosity of vanadium-containing Graham salts (sodium vanadate-phosphate copolymers) as a function of the average degree of polymerization is shown in Table V and in Fig. 4. No change in viscosity with time was observed, presumably because the rate of hydrolysis at the –V–O–P– junctions was very large and because the vanadium containing specimens took a relatively long time to dissolve. As has already been described, the degree of polymerization, $\bar{n}$, of the copolymer is calculated under the assumptions that the polymer chain has been cut off at both sides of the vanadate residue and that the vanadate residue thus cut off does not contribute to the viscosity. Nevertheless, the intrinsic viscosity of vanadium-containing polyphosphates is smaller than that of polyphosphate of the same degree of polymerization, as is shown in Fig. 4.

The fact that vanadate has a smaller intrinsic viscosity than phosphate is demonstrated further by comparing those of ortho salts. Sodium orthovanadate, Na_3VO_4, cannot be obtained by the usual method, but it can be obtained in solution by dissolving sodium metavanadate ($NaVO_3$) in a strongly alkaline solution. An aqueous solution containing 1 N sodium hydroxide and 0.07 N sodium bromide was used as the solvent to measure the intrinsic viscosity. The result was $[\eta]=0.0118$, which was far smaller than the value of sodium orthophosphate (Na_3PO_4) in the same solvent: $[\eta]=0.0530$.

As for the small intrinsic viscosity of the vanadium-containing Graham salts, there may be several reasons. First, comparing curves d and e of Fig. 3, the hydration of vanadium-containing specimens should be smaller than that of vanadium-free specimens. Secondly, the average degree of the polymerization of vanadium-containing specimens might be smaller than the above-estimated values because of some unknown reasons. According to Fig. 4, curves a and b come together if the real $\bar{n}$ value is one-third of the expected value. Actually, paper chromatographic analysis[3)] of solutions of sodium vanadate-phosphate glasses with P/V ratios of 4, 7 and 10 indicated the presence of a relatively large amount of pyrophosphate.

The Time Dependence of Reduced Viscosity. The viscosities of the solutions of samples C and D decreased definitely with time, probably due to the hydrolysis of the branching of the polymer chains[5)].

Since the reduced viscosities (η_{sp}/c) of sodium polyphosphate of various molecular weights at various concentrations has been measured, the curves giving the relationship between the molecular weight and the reduced viscosity at a given concentration can be drawn readily. On the basis of these curves, the data on the time dependence of viscosity can be recalculated to the time dependence of the average molecular weight. It may then be assumed that the rate of hydrolysis is proportional to the number of branching B:

$$-dB/dt=kB \qquad (10)$$

It is also assumed that one molecule is produced by the hydrolysis of one branching, so that the decrease in the number of branching is equal to the increase in the number of molecules, N. Therefore, $-dB=dN$ and $B-B_e=N_e-N$, where B_e and N_e are the values of B and N, respectively, at the end of the hydrolysis. (Probably, $B_e=0$). By assuming further that the average molecular weight, M, is reciprocally proportional to the number of molecules, Eq. 10 can be rewritten and integrated to:

$$\ln(1/M_e-1/M)=-kt+\text{const.} \qquad (11)$$

where M_e is the average molecular weight at the end of hydrolysis, which can be obtained from the reduced viscosity of the solution 20 or 24 hr. after the dissolution. The experimental values were obtained in a thermostat at 25.5°C. Experimental data showed the linear relation expected by Eq. 11. The rate constant of the hydrolysis obtained from the slope of the straight lines was 0.39 hr^{-1}, as is shown in Table VI.

TABLE VI. RATE CONSTANT k OF HYDROLYSIS REACTION AT 25.5°C

Samlpe	Polymer concn. g./100 ml.	NaBr concn. N	k hr^{-1}
C	0.8112	0.035	0.39
	0.3703	0.07	0.39
D	1.0436	0.035	0.39
	1.9165	0.07	0.39

Summary

The intrinsic viscosities of sodium orthophosphates, pyrophosphate, tripolyphosphate and Graham salts of relatively low molecular weight (lower than 10300) were measured. The relation between the intrinsic viscosity at 25.5°C and the average molecular weight measured by the end group titration was

$$[\eta]=6.9\times10^{-4}\times M^{0.61}$$

in a 0.035 N sodium bromide solution, and

$$[\eta]=0.0348+0.112\times10^{-4}\times M$$

in a 0.07 N sodium bromide solution.

Vanadium-containing Graham salts (sodium vanadate-phosphate copolymers) seemed to be hydrolyzed immediately by the dissolution. The intrinsic viscosity of the solution was much smaller than that of sodium polyphosphate of the corresponding degree of polymerization.

The rate of the hydrolysis of branched sodium polyphosphate was proportional to the number of branchings, and the rate constant was 0.39 hr^{-1} at 25.5°C.

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