

Characterization of Ternary (bi-bivalent) Polymetaphosphate Derivatives with Molecular Weight Determination

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ABSTRACT:

Ternary (bi-bivalent) polymetaphosphate derivatives having the composition: $[\text{Na}_x \text{M}^{\text{II}}_{1-x/2a} \text{M}^{\text{III}}_{1-x/2a} \text{PO}_3]_n$ (where M^{II} & M^{III} = Mg (II), Ba (II), Ca (II), Ni (II), Cu (II), Sr (II), Zn (II), $x = 2/3$ & $3/4$, a = valency of metal ion) have been synthesized by fusion technique. Number average molecular weights (M_n) of these derivatives have been determined by end-group titration technique and weight average molecular weights have been determined by intrinsic viscosity measurement in 0.035N NaCl solution. Weight average molecular weights (M_w) obtained by viscosity studies are higher than number average molecular weights (M_n) values indicate their polymeric nature.

Key words: Polymetaphosphate, Fusion technique, Intrinsic viscosity, End-group titration.

INTRODUCTION:

The chemistry of phosphorus compounds has assumed a colossal importance in almost all aspect of human life because of multitudinous applications in the field of fertilizers¹, anti-corrosion agents²⁻³, fire retardants⁴⁻⁶, detergents⁷, flame proofing agents⁸, constituents of paints and inks⁹ and specific radiation sensitive glasses¹⁰⁻¹¹ as well as in better understanding of life-processes. The chemistry of the condense phosphates of alkali metals has been extensively investigated due to the marked stability of their polymeric structure in solution. The condense phosphates of other metals such as alkaline earth, transition and inner transition metals are insoluble solids and consists of long chains of phosphate tetrahedra in several types of structural configurations.

The chief representative of the condense phosphates is Graham's salt, which was prepared by Thomas Graham¹² by thermal dehydration of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. Fleitmann and Henneberg¹³ reported that this product was Hexametaphosphate. Another form of difficultly soluble sodium metaphosphate was obtained by tempering the super-cooled melt of $[\text{NaPO}_3]_n$ at 550°C. Tammann¹⁴ named this derivative as Kurrol's salt. The sequestering ability of Graham's salt towards metal ions was reported by Hall¹⁵, since then it is used for softening of water for boilers and given trade name 'Calgon'. Wall and Doremus¹⁶ reported that the exchange of a part of sodium ion in $[\text{NaPO}_3]_n$ with strontium, does not affect the properties of the former. Mehrotra and Gupta¹⁷ also indicated that if a part of the alkali metal in its phosphates is substituted by bivalent metal ions, the derivative so obtained should have properties similar to that of Graham's salt. This assumption was confirmed by the preparation of soluble complex polymetaphosphate derivatives of the composition $[\text{M}_x^{\text{I}} \text{M}^{\text{II}}_{1-x/a} \text{PO}_3]_n$ (where M^{I} = Li(I), K(I), Cs(I), M^{II} = Mg(II), Ca(II), Ba(II), Zn(II), Cu(II), Ni(II), Pb(II), a = valency of metal ion, $x = 2/3, 1/3, 1/2$). Mehrotra and Vyas later reported soluble complex derivatives of the composition $[\text{K}_x \text{M}^{\text{II}}_{1-x/a} \text{PO}_3]_n$ (where

$M^{II} = \text{Mg(II), Ba(II), Ca(II), Zn(II), Cu(II), Ni(II), Pb(II)}$, $a = \text{valency of metal ion}$, $x = 2/3, 1/3, 1/2$. Similarly Mehrotra and Oza¹⁸ reported soluble complex of derivatives of lithium and cesium polymetaphosphate. All these derivatives are found to be polymeric in nature on the basis of various physico-chemical studies used for characterization of Graham's salt.

The complex polymetaphosphates of the composition $[M_x M^{III}_{1-x/a} PO_3]_n$ where $M^{III} = \text{Pr(III), Nd(III)}$ and $x = 2/3, 1/2, 1/3$, $a = \text{valency of metal ion}$) were synthesized and their polyelectrolytic behaviour and spectral characteristics were studied by Mamta Oza¹⁹. A few complex bimetallic and trimetallic polymetaphosphate derivatives containing alkaline earth and rare earth metals have been synthesized by fusion techniques by Shobhna Sharma²⁰ and characterized by various physico-chemical techniques in these laboratories.

In the present communication, the polymeric nature of ternary complex polymetaphosphate derivatives of the composition: $[Na_x M^{II}_{1-x/2a} M^{II}_{1-x/2a} PO_3]_n$ (where $M^{II} \& M^{II} = \text{Mg (II), Ba (II), Ca (II), Ni (II), Cu (II), Sr (II), Zn (II)}$, $x = 2/3, 3/4$, $a = \text{valency of metal ion}$) have been characterized with molecular weight determination have been recorded.

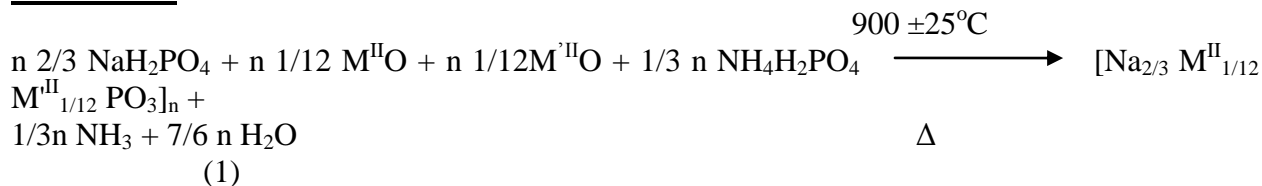
MATERIAL AND METHODS:

All the reagents such as NaH_2PO_4 , $NH_4H_2PO_4$ and metal oxides used were of analytical grade. Double distilled water used for preparing the solutions. An Ostwald viscometer having efflux time between 80-120 sec. for water was used for viscosity measurements and a Pycknometer of volume about 10 ml was used for density measurements. A digital pH- meter having glass and a calomel electrode was used for pH measurements. Viscosity measurements were performed at $30 \pm 0.1^\circ\text{C}$. All the measurements were carried out after 24 hours of dissolution so as to attain equilibrium.

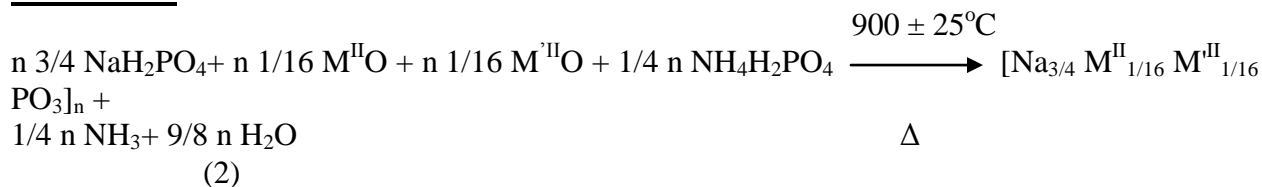
PREPARATION:

Complex polymetaphosphate derivatives of the composition $[Na_x M^{II}_{1-x/2a} M^{II}_{1-x/2a} PO_3]_n$ (where $M^{II} \& M^{II} = \text{Mg (II), Ba (II), Ca (II), Ni (II), Cu (II), Sr (II), Zn (II)}$, $x = 2/3, 3/4$, $a = \text{valency of metal ion}$) were prepared by fusion technique in accordance with the equation (1) & (2).

When $x=2/3$



When $x=3/4$



The reactant were taken in a platinum crucible, heated over a flame for 40-45 minutes and then put in a muffle furnace at $800 \pm 25^\circ\text{C}$ for one hour. A clear melt was obtained in almost all the cases which was then chilled between cold stainless steel plates to give a clear glass. The colour of the glass was green in the case of copper derivatives whereas in all the other cases it was colourless. The yield was almost theoretical and the composition was confirmed by estimating phosphorous and metal contents of the compounds.

Phosphorous was estimated volumetrically as ammonium molybdate and metals by standard methods as described by Vogel²¹ given in table (1).

Table: 1 Analysis of complex polymetaphosphate derivatives: The complex polymetaphosphates synthesized as above were analyzed for their constituents i.e. Phosphorus, Alkali Metals, Bivalent Metals for the confirmation of their compositions.

Sr. No	Complex Polymetaphosphates	% P		% of M ^I		% of M ^{II}		% of M ^{III}	
		Exp	Cal.	Exp	Cal.	Exp	Cal.	Exp	Cal.
1	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ba}_{1/12} \text{PO}_3]_n$	28.70	28.75	14.17	14.21	1.79	1.87	10.58	10.61
2	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ca}_{1/12} \text{PO}_3]_n$	31.02	31.09	15.30	15.37	2.00	2.03	3.30	3.34
3	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ni}_{1/12} \text{PO}_3]_n$	30.58	30.62	15.11	15.13	1.88	2.00	4.78	4.83
4	$[\text{Na}_{2/3} \text{Ba}_{1/12} \text{Ca}_{1/12} \text{PO}_3]_n$	28.36	28.41	14.01	14.04	10.40	10.48	3.02	3.06
5	$[\text{Na}_{3/4} \text{Ba}_{1/16} \text{Ca}_{1/16} \text{PO}_3]_n$	28.66	28.88	16.01	16.06	7.89	7.99	2.30	2.33
6	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ba}_{1/16} \text{PO}_3]_n$	29.07	29.14	16.27	16.21	1.38	1.42	8.00	8.07
7	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ca}_{1/16} \text{PO}_3]_n$	30.20	30.91	17.10	17.19	1.48	1.51	2.42	2.49
8	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	30.36	30.43	16.86	16.92	1.42	1.49	4.20	4.03
9	$[\text{Na}_{3/4} \text{Ca}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	30.04	30.14	16.72	16.76	2.38	2.40	2.90	3.99
10	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ni}_{1/16} \text{PO}_3]_n$	30.36	30.56	16.90	16.99	1.42	1.49	3.58	3.61
11	$[\text{Na}_{3/4} \text{Ba}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	28.33	28.46	15.78	15.83	7.82	7.88	3.72	3.77
12	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Cu}_{1/16} \text{PO}_3]_n$	30.35	30.46	16.90	16.94	1.42	1.49	3.85	3.90
13	$[\text{Na}_{3/4} \text{Zn}_{1/16} \text{Sr}_{1/16} \text{PO}_3]_n$	27.72	27.78	15.40	15.46	3.62	3.68	4.85	4.91

Molecular Weight Determination:

The molecular weights of these simple and complex polymetaphosphate derivatives are termed as average molecular weights and not absolute molecular weights, as these compounds are a mixture of macromolecular chains with different degree of polymerization. The expression of the molecular weight of the polymer as an average is a practical necessity because it depends

upon the nature of the product property used for its determination. In the limiting cases, the complex polymetaphosphate glasses have both the branched and linear polymer regions. If the polymers are linear and metal to phosphorous ratio is exactly one, then the chain length should be infinite. Therefore, the molecular weights determined by two methods are used as averages: The molecular weights of these polymers are usually expressed as:

Number average molecular weight (M_n) and Weight average molecular weight (M_w)

Number average molecular weight (M_n): The Number average molecular weight is the sum of the weights of the individual molecules divided by their total number. Hence, M_n is expressed by the equation:

$$M_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \dots}{N_1 + N_2 + N_3 + \dots} \quad (3)$$

or

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \quad (4)$$

Where N_i is the number and M_i is the molecular weight of the species.

Weight average molecular weight (M_w): If the properties such as light scattering, sedimentation and dialysis, which depend not only on the concentration but also on the weight of the particles, are used for molecular weight determination, the average obtained called as weight average molecular weight (M_w) and is given by the equation:

$$M_w = \frac{W_1M_1 + W_2M_2 + W_3M_3 + \dots}{N_1 + N_2 + N_3 + \dots} \quad (5)$$

Since $W_i = N_i M_i$
Hence,

$$M_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \dots}{N_1 + N_2 + N_3 + \dots} \quad (6)$$

or

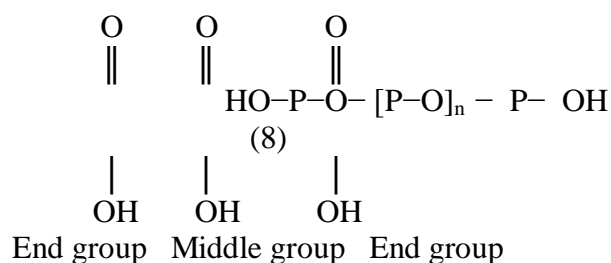
$$M_w = \frac{\sum N_i M_i^2}{\sum N_i} \quad (7)$$

where N_i is the number and M_i is the molecular weight of the species.

If in a polymer, all the chains are of equal length, then $M_w = M_n$ and it is a hypothetical monodispersed system. However, for polydispersed system M_w is greater than M_n and their ratio increases as the range of the size of chains increases. Thus, the ratio M_w to M_n is a measure of polydispersity of the polymer in the system.

End-group titration:

End-group titration is probably the most useful method of analysis for the polyphosphates, because the end-groups can be determined independently by a direct titration between the end points near pH 4.5-9.5. A chain like structure containing $(PO_3)_n^{n-}$ units was proposed as:



Because, in the long chain of polyphosphates, middle groups are strongly acidic and end groups are weakly acidic in nature. In middle groups, two oxygen atoms of each of the phosphate (PO_4) tetrahedron are shared with neighboring tetrahedron and the end groups shared only one oxygen atom with adjacent PO_4 tetrahedron in the chain. The strongly acidic middle groups can be titrated with alkali upto 4.5 pH whereas end groups in between pH 4.5-9.5.

Determination of the number average molecular weights (M_n):

The number average molecular weights of these derivatives were determined by end-group titration technique. The pH of the solution was adjusted to nearly 3.0 by adding 0.01M HCl and then it was titrated with standard 0.01M NaOH upto pH 9-10. Assuming that there is one acidic hydroxyl group at each end of the polymer chain, the titration of these requires two equivalents of alkali per gram mole of the polymer. The number average molecular weight (M_n) is given by the equation:

$$(9) \quad M_n = \frac{20,000 \times \text{Amount of sample taken in gms.}}{\text{Vol. of 0.1N NaOH used in the pH range}}$$

In these calculations, it is assumed that these complex derivatives do not contain any cyclic phosphates. This has been confirmed by thin layer chromatographic studies of these derivatives, IR studies, NMR studies etc. Moreover the cyclic phosphates of bivalent metal ions are insoluble whereas all these derivatives are soluble in water.

Viscosity studies: The complex polymetaphosphate derivatives are characterized with the help of various physico-chemical techniques. Out of these, viscosity is used to measure the size or extension of a polymer molecule in the given space. Empirically, it is related to molecular

weights for linear polymers only. Due to simplicity of measurements and full accuracy, it is a popular technique for the determination of weight average molecular weight of long chain polymers including polyphosphates.

Determination of the weight average molecular weights (M_w):

Weight average molecular weights (M_w) were determined by intrinsic viscosity measurement in 0.035 N NaCl solutions. The intrinsic viscosity $(\eta_{sp}/C)_{C \rightarrow 0}$ is given by the equation:

$$(\eta_{sp}/C)_{C \rightarrow 0} = K M_w \quad (10)$$

where $\eta_{sp} = \eta_s / \eta_o$, η_s and η_o are the viscosities of the solution and the solvent respectively and C is the concentration of the polymer in gm/100ml. The polymer concentration was taken in the range of 0.2 to 0.8 gm/100ml. The accuracy of these results is of the order of ± 5 percent.

η_{sp}/C is plotted against concentration, a straight line is obtained, the extrapolation of which gives the reduced viscosity. The value of K is given as 1.76×10^{-5} by Strauss²³ by light scattering measurements for sodium polymetaphosphate in sodium bromide solution. It is already pointed out that the sodium and lithium polymetaphosphate solution show a similar behaviour.

Strauss and Coworkers have determined the molecular weights of lithium polymetaphosphate by intrinsic viscosity measurements in sodium bromide and lithium bromide solutions and have observed that the values fall within the range of the molecular weights obtained by light scattering studies.

Result and Discussions:

End-group titration:

The end-group titration curves for complex polymetaphosphates of the composition $[Na_x M^{II}_{1-x/2a} M^{II}_{1-x/2a} PO_3]_n$ (where M^{II} & $M^{II} = Mg(II), Ba(II), Ca(II), Ni(II), Cu(II), Sr(II), Zn(II)$, $x = 2/3, 3/4$, $a =$ valency of metal ion) are given in figure (1).

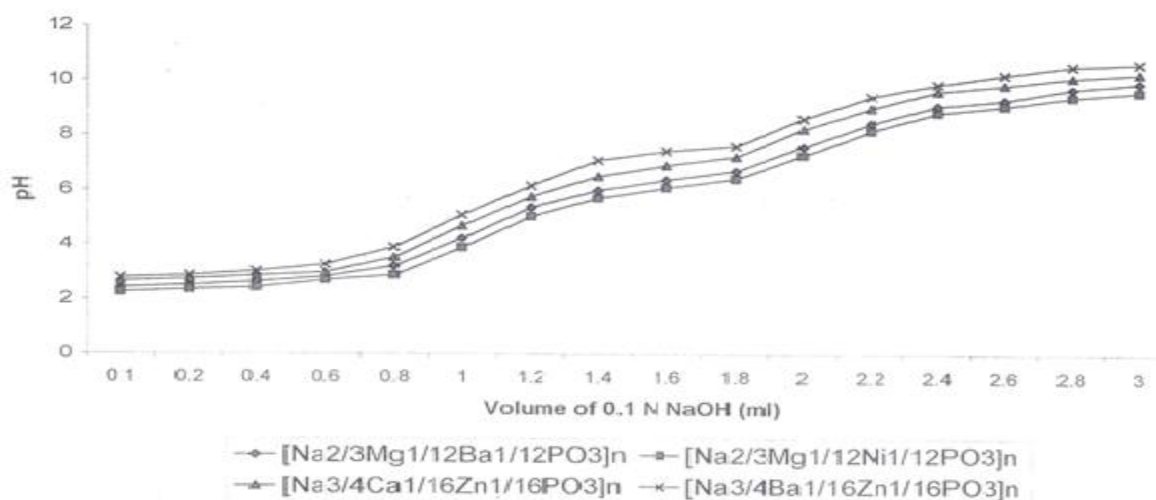


Figure 1: pH metric titration curve of various complex polymetaphosphates with 0.1N NaOH

In the titration curves the amount of 0.1N NaOH used between two inflection curves was employed for calculating the M_n and these values are recorded in table (2). Each of these titration curves shows two inflection points, the first at about pH 4.5 and another around pH 9.5 units. The presence of these two inflections is indicative of the presence of strongly acidic middle and weakly acidic end groups. The nature of these curves and inflections is similar to those obtained in case of Graham's salt and poly (lithium phosphate). Similar types of curves were also obtained by Mehlotra et al²⁴ in case of the poly (lithium/sodium phosphates).

Table: 2 Number average molecular weight (M_n) determined by end- group titration

Sr. No.	Complex Polymetaphosphate	W (in gm.)	V (in ml)	M_n
1	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ba}_{1/12} \text{PO}_3]_n$	0.1025	0.62	3306
2	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ca}_{1/12} \text{PO}_3]_n$	0.1030	0.52	3962
3	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ni}_{1/12} \text{PO}_3]_n$	0.1022	0.42	4866
4	$[\text{Na}_{2/3} \text{Ba}_{1/12} \text{Ca}_{1/12} \text{PO}_3]_n$	0.1030	0.56	3678
5	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ba}_{1/16} \text{PO}_3]_n$	0.1020	0.50	4080
6	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ca}_{1/16} \text{PO}_3]_n$	0.1052	0.60	3507
7	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	0.1018	0.44	4628
8	$[\text{Na}_{3/4} \text{Ca}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	0.1022	0.72	2839
9	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ni}_{1/16} \text{PO}_3]_n$	0.1002	0.41	4888
10	$[\text{Na}_{3/4} \text{Ba}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	0.1035	0.58	3569
11	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Cu}_{1/16} \text{PO}_3]_n$	0.1015	0.48	4230
12	$[\text{Na}_{3/4} \text{Ba}_{1/16} \text{Ca}_{1/16} \text{PO}_3]_n$	0.1010	0.46	4392
13	$[\text{Na}_{3/4} \text{Zn}_{1/16} \text{Sr}_{1/16} \text{PO}_3]_n$	0.1016	0.50	4064

W= weight of the polymer sample used in titration

V= Volume of 0.1N NaOH consumed between 4.5- 9.5 pH

As the nature of the titration curves is similar to those of Graham's salt, it can be concluded that the polymetaphosphate derivatives consist of end and middle groups in the chain like polymeric anion.

The number average molecular weight calculated according to the equation (9) is given in the table (2). A perusal of the data of the tables would show that the M_n values of the derivatives having $x = 2/3$ in the composition $[\text{Na}_x \text{M}^{\text{II}}_{1-x/2a} \text{M}^{\text{II}}_{1-x/2a} \text{PO}_3]_n$ were found to be in the range 3306-4866. The chain length for these derivatives corresponding to ~ 30-40 units. The M_n values of these derivatives with $x = 3/4$ in the above composition were found to be in the range 2839 – 4888. The chain length for these derivatives correspondence to 25-40 units.

In fact the M_n values for complex polymetaphosphates are less than half the weight average molecular weight of Graham's salt prepared under similar conditions. It appears that complex polymetaphosphates consists of bi- or tri-polyanionic chains of $(\text{PO}_3)_n^{-n}$ bonded through polyvalent cations, thereby reducing the number of polyanions in solutions. Therefore, number

average molecular weights of complex polymetaphosphates are lower than those of simple polymetaphosphates.

In final conclusions, it can be stated that:

1. The M_n values for the complex polymetaphosphates depends upon the value of x .
2. Comparatively the M_n values for complex polymetaphosphates are in general lower than those of Graham's salt.
3. The M_n values of these derivatives lie in the range 2500-5000, indicating a chain length equal to 25-50 units. These values are also in the same range as found in case of poly (alkaline earth – alkali metal phosphates) reported by Mehrotra & Oza²³.

Viscosity studies:

The viscosity measurements of the complex polymetaphosphate derivatives of the composition:

$[\text{Na}_x \text{M}^{\text{II}}_{1-x/2a} \text{M}^{\text{II}}_{1-x/2a} \text{PO}_3]_n$ were measured by Ostwald viscometer in 0.035N NaCl solution support the linear polymeric character of these derivatives. Reduced and inherent viscosity (η_{sp}/C & $\ln \eta_r/C$) of these derivatives are given in table (3). The plot of reduced viscosity (η_{sp}/C) and inherent viscosity ($\ln \eta_r/C$) with respect to concentration, for these derivatives are straight lines are given in figure (2)

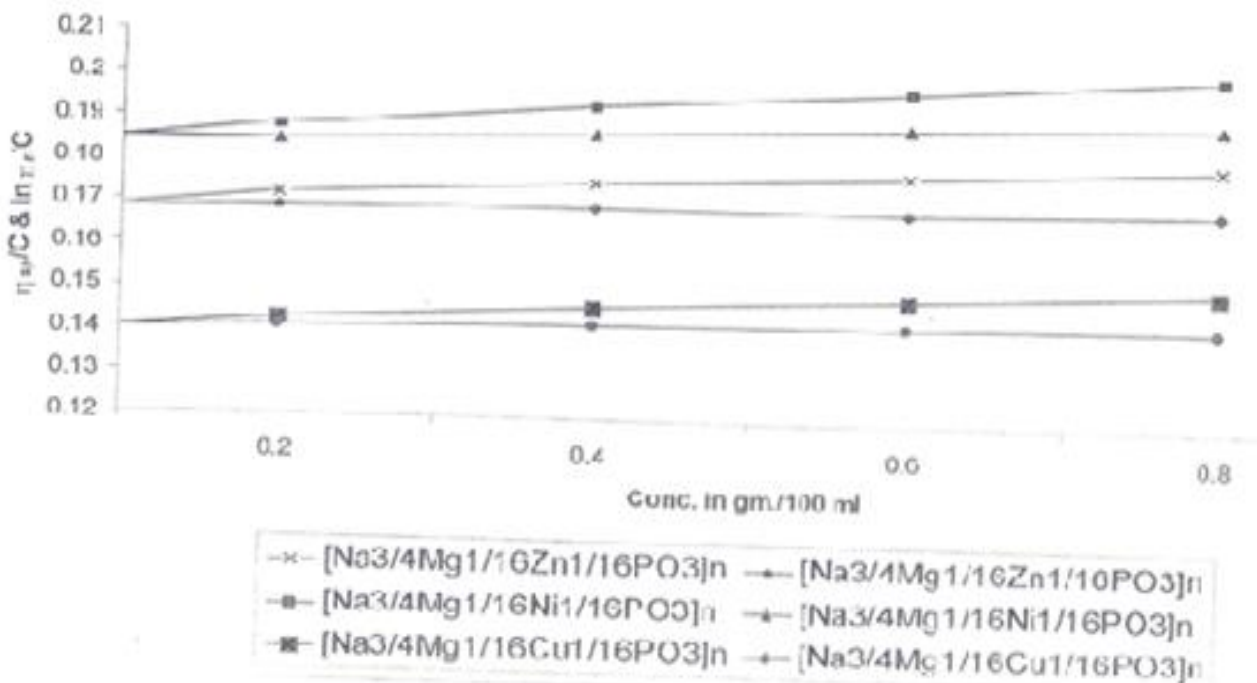


Figure 2: Plots of η_{sp}/C and $\ln \eta_r/C$ Vs Concentration

The straight lines curves of these viscosities extrapolate to the same point on Y- axis at zero concentration. The straight line curves of similar nature were also obtained by Vyas et al²⁴ for poly (ammonium/ amidium phosphates). This type of behaviour is characteristic of linear polymer as suggested by Maron²⁵ and Mead et. al²⁶.

Table: 3 Viscosity studies in 0. 035 N Sodium Chloride

Sr. No.	Complex Polymetaphosphate	Concentration gm/100ml	η_{sp}/C	$\ln\eta_r/C$	F	G
1	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ba}_{1/12} \text{PO}_3]_n$	0.2	0.1143	0.1130	0.25	0.1428
		0.4	0.1170	0.1143	0.66	0.1950
		0.6	0.1214	0.1172	1.50	0.3035
		0.8	0.1251	0.1193	4.00	0.6255
2	$[\text{Na}_{2/3} \text{Mg}_{1/12} \text{Ca}_{1/12} \text{PO}_3]_n$	0.2	0.1409	0.1390	0.25	0.1761
		0.4	0.1440	0.1400	0.66	0.2400
		0.6	0.1468	0.1407	1.50	0.3670
		0.8	0.1496	0.1414	4.00	0.7480
3	$[\text{Na}_{2/3} \text{Ba}_{1/12} \text{Ca}_{1/12} \text{PO}_3]_n$	0.2	0.1310	0.1294	0.25	0.1637
		0.4	0.1337	0.1303	0.66	0.2228
		0.6	0.1364	0.1311	1.50	0.3410
		0.8	0.1392	0.1320	4.00	0.6960
4	$[\text{Na}_{3/4} \text{Ba}_{1/16} \text{Ca}_{1/16} \text{PO}_3]_n$	0.2	0.1454	0.1434	0.25	0.1817
		0.4	0.1485	0.1442	0.66	0.2475
		0.6	0.1513	0.1449	1.50	0.3782
		0.8	0.1529	0.1443	4.00	0.7645
5	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ca}_{1/16} \text{PO}_3]_n$	0.2	0.1271	0.1255	0.25	0.1588
		0.4	0.1297	0.1265	0.66	0.2161
		0.6	0.1323	0.1274	1.50	0.3307
		0.8	0.1351	0.1283	4.00	0.6755
6	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	0.2	0.1722	0.1694	0.25	0.2152
		0.4	0.1756	0.1697	0.66	0.2926
		0.6	0.1785	0.1696	1.50	0.4462
		0.8	0.1832	0.1710	4.00	0.9160
7	$[\text{Na}_{3/4} \text{Ca}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	0.2	0.0994	0.0985	0.25	0.1243
		0.4	0.1019	0.0999	0.66	0.1698
		0.6	0.1049	0.1017	1.50	0.2623
		0.8	0.1079	0.1035	4.00	0.5395
8	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Ni}_{1/16} \text{PO}_3]_n$	0.2	0.1881	0.1847	0.25	0.2351
		0.4	0.1944	0.1872	0.66	0.3240
		0.6	0.2008	0.1896	1.50	0.5020
		0.8	0.2070	0.1916	4.00	1.0350
9	$[\text{Na}_{3/4} \text{Ba}_{1/16} \text{Zn}_{1/16} \text{PO}_3]_n$	0.2	0.1265	0.1249	0.25	0.1581
		0.4	0.1296	0.1264	0.66	0.2160
		0.6	0.1325	0.1276	1.50	0.3312
		0.8	0.1354	0.1286	4.00	0.6770
10	$[\text{Na}_{3/4} \text{Mg}_{1/16} \text{Cu}_{1/16} \text{PO}_3]_n$	0.2	0.1430	0.1410	0.25	0.1787
		0.4	0.1463	0.1422	0.66	0.2938
		0.6	0.1493	0.1430	1.50	0.3732
		0.8	0.1523	0.1437	4.00	0.7615
11	$[\text{Na}_{3/4} \text{Ba}_{1/16} \text{Ca}_{1/16} \text{PO}_3]_n$	0.2	0.1402	0.1383	0.25	0.1752
		0.4	0.1434	0.1394	0.66	0.2390
		0.6	0.1463	0.1402	1.50	0.3657
		0.8	0.1495	0.1412	4.00	0.7475

These straight line curves show that relationship between reduced and inherent viscosity is a function of concentration, which can be expressed by Huggin's equation:

$$\eta_{sp}/C = \eta + K' \eta^2 C \quad (11)$$

$$\ln \eta_r/C = \eta + K'' \eta^2 C \quad (12)$$

where K' and K'' are constants and sum of these constants ($K' + K''$) for long chain polymers²⁷ is equal to 0.5. However, the values ranging from 0.49 to 0.58 have been obtained for these complex polymetaphosphate derivatives.

The weight average molecular weights have been calculated from viscosity data in 0.035N NaCl solution with the help of Staudinger equation:

$$\eta = K M_w \quad (13)$$

where $K = 1.76 \times 10^{-5}$ was determined by Strauss et al²². The values of M_w obtained in this manner are given in table (4). The intrinsic viscosity (η) used in the above equation was determined from the plots of specific or reduced viscosity versus concentration of polymetaphosphate derivatives. From the graph it can be observed that the deviation from the straight line exists particularly at lower concentration. This deviation has been attributed to an increased negative charge on polyanion due to uncoiling in presence of swamping electrolyte and hence, extrapolation can not be obtained with high accuracy. However this difficulty has been overcome by using a recently modified method for calculation of intrinsic viscosity from reduced viscosity data for high molecular weight polymer by Nagy et al²⁸.

This new graphical method provides a common error distribution in determination of specific viscosity of the polymer solution at high dilutions. It ensures that the extrapolation to zero concentration is more feasible and gives better values of intrinsic viscosity which can be used with more certainty.

The extrapolation of usual straight line relationship:

$$Y = aX + b \quad (14)$$

is replaced with the extrapolation of the linear transformation:

$$G = AF + B \quad (15)$$

where the variables G & F are defined as:

$$G = Y/\alpha - X \text{ \& } F = X/\alpha - X \quad (16)$$

where $Y = \eta_{sp}/C$, X = concentration, α = sum of minimum and maximum concentration i.e. $X_m + X_M$. The parameters A (slope) and B (intercept) are used for the calculation of 'a' and 'b'.

$$A = A - B \text{ and } b = B \alpha \quad (17)$$

The value of 'b' corresponds to improved values of intrinsic viscosity determined with the help of equation (17). The improved values of $[\eta]$ is designated as $[G_n]$ for the purpose of differentiating the two terms from each other. η is obtained by the usual plots of η_{sp}/C versus concentration, whereas $[G_n]$ is obtained from equation (19). The improved values of M_w^* can be calculated by using the equation:

$$\lim_{C \rightarrow 0} [G_n] = \frac{\eta}{X_m + X_M} \quad (18)$$

Therefore,

$$(X_m + X_M) \lim_{C \rightarrow 0} [G] = [G_n] = 1.76 \times 10^{-5} \times M_w^* \quad (19)$$

The values for $[\eta]$ are obtained from η_{sp}/C versus concentration plots and $[G_n]$ obtained from equation (19). The values of $[\eta]$ and $[G_n]$ differ by 2-5% only.

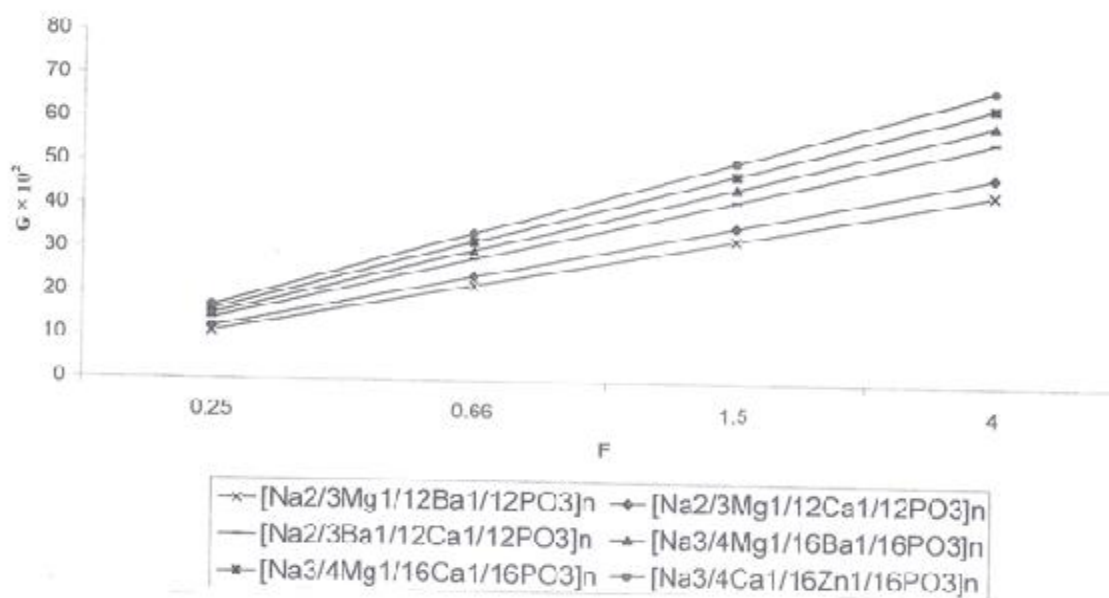


Figure 3: Plots of Factor G Vs F

Molecular weight distribution:

The ratio of M_w/M_n lies in the range 1.74-2.11 for these derivatives. Van-wazer²⁹ and Newman³⁰ reported a M_w/M_n ratio equivalent to 2.0 in case of long chain polymers and inferred that such polymers have a Poisson distribution suggested by Flory³¹, while considering the random reorganization in linear organic polymers. It was suggested that terminal phosphate groups of the P-O-P chain are not involved in the reorganization process.

Ohashi et al³² determined the viscosity of Graham's salt. It has been stated that distribution of molecular weight is not exactly the Poisson distribution for lower molecular weight (<1000) samples. In general for a polydispersed polymers, the differences in the various types of average molecular weights increase in the order such as $M_w > M_n$.

The ratio M_w/M_n for these polymers is also more than two. Therefore, it can be predicted that molecular weight distribution for polyphosphate derivatives is not exactly Poisson distribution as expected in case of linear chain polymers. In fact the terminal phosphate groups of

P-O-P chains are involved in reorganization process, since the Poisson distribution is indicated for middle group titration studies.

The ratio M_w/M_n complex polymetaphosphate derivatives are given in table (4). Usually the molecular weights of long chain polyphosphates follow a Poisson distribution. The M_w values for these derivatives are twice of the M_n values. A slight variation from this ratio is therefore indicative of some error in the determined of the M_n values by end-group titration method. The corrected values for M_n may be calculated from corrected intrinsic viscosity $[G_n]$ using the equation:

$$(X_m + X_M)[G_n] = 3.52 \times 10^{-5} \times M_n^* \quad (20)$$

where 3.52×10^{-5} corresponds to $2K$, the constant used by Strauss²³ in Staudinger equation. The corrected values of M_n are recorded in table (4) have been compared with the values determined by end-group titrations, these values differ from the experimentally determined M_n by 10-15%.

Table: 4 Number Average & Weight Average Molecular Weight Determination of Complex Polymetaphosphates

Sr. No.	Complex Polymetaphosphates	M_n	M_w	M_n^*	M_w^*	M_w/M_n
1	$[Na_{2/3} Mg_{1/12} Ba_{1/12} PO_3]_n$	3306	6307	3153	6478	1.90
2	$[Na_{2/3} Mg_{1/12} Ca_{1/12} PO_3]_n$	3962	7841	3920	7955	1.97
3	$[Na_{2/3} Mg_{1/12} Ni_{1/12} PO_3]_n$	4866	8662	4886	8778	1.78
4	$[Na_{2/3} Ba_{1/12} Ca_{1/12} PO_3]_n$	3678	7273	3636	7387	1.98
5	$[Na_{3/4} Ba_{1/16} Ca_{1/16} PO_3]_n$	4392	7841	3920	7898	1.78
6	$[Na_{3/4} Mg_{1/16} Ba_{1/16} PO_3]_n$	4080	8125	4062	8239	1.99
7	$[Na_{3/4} Mg_{1/16} Ca_{1/16} PO_3]_n$	3507	7046	3523	7216	2.00
8	$[Na_{3/4} Mg_{1/16} Zn_{1/16} PO_3]_n$	4628	9546	4773	9660	2.06
9	$[Na_{3/4} Ca_{1/16} Zn_{1/16} PO_3]_n$	2839	5512	2756	5625	1.94
10	$[Na_{3/4} Mg_{1/16} Ni_{1/16} PO_3]_n$	4888	10341	5170	10455	2.11
11	$[Na_{3/4} Ba_{1/16} Zn_{1/16} PO_3]_n$	3569	6989	3494	7103	1.95
12	$[Na_{3/4} Mg_{1/16} Cu_{1/16} PO_3]_n$	4230	7955	3948	8125	1.88
13	$[Na_{3/4} Zn_{1/16} Sr_{1/16} PO_3]_n$	4064	8125	4148	8296	1.99

The ratio M_w/M_n determined in case of complex polymetaphosphate derivatives of the composition:

$[Na_x M^{II}_{1-x/2a} M^{II}_{1-x/2a} PO_3]_n$ described in table (4) lies in the range as observed for poly (lithium phosphates) and Graham's salt. Therefore, it can be concluded that these derivatives are

polymeric in nature similar to that observed in case of poly (lithium phosphates) and Graham's salt.

Conclusions:

The high molecular weights of all these derivatives obtained by end-group titration and intrinsic viscosity measurement in 0.035N NaCl solution method shows that they are polymeric in nature.

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