

Characterization of Ternary (Bi-Trivalent) Polymetaphosphate Derivatives with Molecular Weight Determination

Vishnu Kumar Khandelwal

Chemistry department

vishnumec1974@gmail.com

Jaipur engineering college & research centre, Jaipur, Rajasthan-India

Abstract: Ternary (bi-trivalent) polymetaphosphate derivatives having the composition $[\text{Na}_x\text{M}^{\text{III}}_{1-x/2a}\text{M}^{\text{II}}_{1-x/2a}\text{PO}_3]_n$ (where $\text{M}^{\text{II}} = \text{Mg(II), Ba(II), Ca(II), Ni(II), Cu(II), Sr(II), Zn(II)}$, $\text{M}^{\text{III}} = \text{Fe(III), La(III), Sm(III), Gd(III)}$, $x = 2/3, 3/4$, $a =$ 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: End group titration, Fusion Technique, intrinsic viscosity, polymetaphosphates.

1. INTRODUCTION

The condensed phosphates form a very important class of phosphorous compounds which exhibit marked stability of polymeric structure in solution. Structurally, condensed phosphates include all those compounds of P-O-P linkage formed by the sharing of PO_4 tetrahedra, in cyclic chain or cross-linked structures. Specifically the polyphosphates consist of PO_4 tetrahedra sharing two of their oxygen atoms with adjoining PO_4 tetrahedra forming long chain polyanions of the formulation $(\text{PO}_3)_n^{-n}$. These polyanionic chains exhibit pronounced capacity for sequestration of metal ions.

The chief representative of the condense phosphates is Graham's salt, which was prepared by Thomas Graham¹ by thermal dehydration of $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$. Fleitmann and Henneberg² 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 . Tammann³ named this derivative as Kurrol's salt. The sequestering ability of Graham's salt towards metal ions was reported by Hall⁴, since then it is used for softening of water for boilers and given trade name 'Calgon'. Wall and Doremus⁵ 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 Gupta⁶ 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 $\text{M}^{\text{I}} = \text{Li(I), K(I), Cs(I)}$, $\text{M}^{\text{II}} = \text{Mg(II), Ca(II), Ba(II), Zn(II), Cu(II), Ni(II), Pb(II)}$, $a =$ 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 $\text{M}^{\text{II}} = \text{Mg(II), Ba(II), Ca(II), Zn(II), Cu(II), Ni(II), Pb(II)}$, $a =$ valency of metal ion, $x = 2/3, 1/3, 1/2$). Similarly Mehrotra and Oza⁷ 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 $[\text{M}_x^{\text{I}}\text{M}^{\text{III}}_{1-x/a}\text{PO}_3]_n$ where $\text{M}^{\text{III}} = \text{Pr(III), Nd(III)}$ and $x = 2/3, 1/2, 1/3$, $a =$ valency of metal ion) were synthesized and their polyelectrolytic behaviour and spectral characteristics were studied by Mamta Oza⁸. A few complex bimetallic and trimetallic polymetaphosphate derivatives containing alkaline earth and rare earth metals have been synthesized by fusion techniques by Shobhna Sharma⁹ 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: $[\text{Na}_x\text{M}^{\text{III}}_{1-x/2a}\text{M}^{\text{II}}_{1-x/2a}\text{PO}_3]_n$ (where $\text{M}^{\text{II}} = \text{Mg(II), Ba(II), Ca(II), Ni(II), Cu(II), Sr(II), Zn(II)}$, $\text{M}^{\text{III}} = \text{Fe(III), La(III), Sm(III), Gd(III)}$, $x = 2/3, 3/4$, $a =$ Valency of metal ion) have been characterized with molecular weight determination have been recorded.

2. MATERIAL AND METHODS

All the reagents such as NaH_2PO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ 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 $30^{\circ} \pm 0.1^{\circ}\text{C}$. All the measurements were carried out after 24 hours of dissolution so as to attain equilibrium.

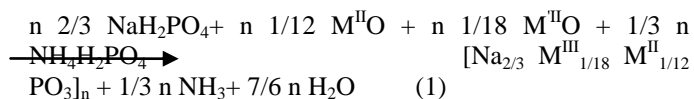
3. PREPARATION

Preparation of complex polymetaphosphate derivatives of the composition $[\text{Na}_x\text{M}^{\text{III}}_{1-x/2a}\text{M}^{\text{II}}_{1-x/2a}\text{PO}_3]_n$ (where $\text{M}^{\text{II}} = \text{Mg}(\text{II}), \text{Ba}(\text{II}), \text{Ca}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Sr}(\text{II}), \text{Zn}(\text{II}), \text{M}^{\text{III}} = \text{Fe}(\text{III}), \text{La}(\text{III}), \text{Sm}(\text{III}), \text{Gd}(\text{III}), x = 2/3, 3/4, a = \text{Valency of metal ion})$

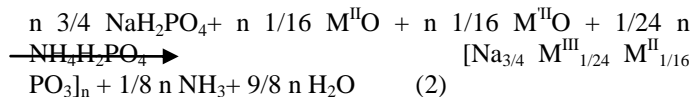
When $x = 2/3$

polymetaphosphate derivatives of the composition $[\text{Na}_x\text{M}^{\text{III}}_{1-x/2a}\text{M}^{\text{II}}_{1-x/2a}\text{PO}_3]_n$ (where $\text{M}^{\text{II}} = \text{Mg}(\text{II}), \text{Ba}(\text{II}), \text{Ca}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II}), \text{Sr}(\text{II}), \text{Zn}(\text{II}), \text{M}^{\text{III}} = \text{Fe}(\text{III}), \text{La}(\text{III}), \text{Sm}(\text{III}), \text{Gd}(\text{III}), x = 2/3, 3/4, a = \text{Valency of metal ion})$ were prepared by fusion technique in accordance with the equation (1) & (2).

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 color of the glass was



When $x = 3/4$



green in the case of copper derivatives whereas in all the other cases it was colorless. 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 Vogel¹⁰ 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, Trivalent Metals
for the confirmation of their compositions

S. No	Complex Polymetaphosphates	% P		% of M^{I}		% of M^{II}		% of M^{III}	
		Exp	Cal.	Exp	Cal.	Exp	Cal	Exp	Cal
1	$[\text{Na}_{3/4} \text{Fe}_{1/24} \text{Mg}_{1/16} \text{PO}_3]_n$	30.84	30.9	17.1	17.2	1.45	1.5	2.2	2.3
2	$[\text{Na}_{3/4} \text{Fe}_{1/24} \text{Zn}_{1/16} \text{PO}_3]_n$	30.06	30.1	16.7	16.7	3.85	3.9	2.2	2.2
3	$[\text{Na}_{3/4} \text{Fe}_{1/24} \text{Ca}_{1/16} \text{PO}_3]_n$	30.35	30.6	17.0	17.0	2.40	2.4	2.2	2.3
4	$[\text{Na}_{3/4} \text{La}_{1/24} \text{Mg}_{1/16} \text{PO}_3]_n$	29.90	29.9	16.6	16.6	1.40	1.4	5.5	5.5
5	$[\text{Na}_{2/3} \text{La}_{1/18} \text{Zn}_{1/12} \text{PO}_3]_n$	28.80	28.8	14.2	14.2	5.00	5.0	7.1	7.1
6	$[\text{Na}_{2/3} \text{Sm}_{1/18} \text{Ba}_{1/12} \text{PO}_3]_n$	27.00	27.0	20.0	20.0	9.85	9.9	7.2	7.2

4. 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:

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

or

$$M_n = \frac{\sum NiMi}{\sum Ni} \tag{4}$$

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:

$$M_w = \frac{W_1M_1 + W_2M_2 + W_3M_3 + \dots}{W_1 + W_2 + W_3 + \dots} \tag{5}$$

Since $W_i = N_iM_i$

Hence,

$$M_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \dots}{N_1M_1 + N_2M_2 + N_3M_3 + \dots}$$

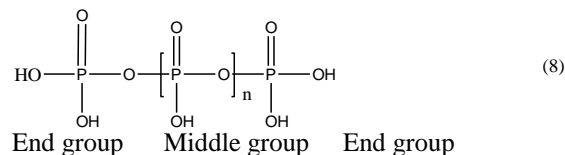
$$M_w = \frac{\sum NiMi^2}{\sum Ni} \tag{7}$$

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 $(PO_3)_n$ 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.

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 Strauss¹¹ 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.

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.

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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.

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:

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

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 Strauss¹¹ 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.

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

5. RESULT AND DISCUSSION

End-group titration:

The end-group titration curves for complex polymetaphosphates of the composition: $[\text{Na}_x\text{M}^{\text{III}}_{1-x/2a}\text{M}^{\text{III}}_{1-x/2a}\text{PO}_3]_n$ (where M^{III} & $\text{M}^{\text{III}} = \text{Fe(III)}, \text{La(III)}, \text{Sm(III)}, \text{Gd(III)}$, $x = 2/3, 3/4$, $a =$ Valency of metal ion) are given in figure (1).

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 al¹² in case of the poly (lithium/sodium phosphates).

S. No.	Complex Polymetaphosphate	W (in gm.)	V (in ml)	M_n
1	$[\text{Na}_{3/4}\text{Fe}_{1/24}\text{Mg}_{1/16}\text{PO}_3]_n$	0.1005	0.62	3242
2	$[\text{Na}_{3/4}\text{Fe}_{1/24}\text{Zn}_{1/16}\text{PO}_3]_n$	0.1112	0.47	4732
3	$[\text{Na}_{3/4}\text{Fe}_{1/24}\text{Ca}_{1/16}\text{PO}_3]_n$	0.1008	0.78	2585
4	$[\text{Na}_{3/4}\text{La}_{1/24}\text{Mg}_{1/16}\text{PO}_3]_n$	0.1020	0.80	2550
5	$[\text{Na}_{2/3}\text{La}_{1/18}\text{Zn}_{1/12}\text{PO}_3]_n$	0.1011	0.64	3160
6	$[\text{Na}_{2/3}\text{Sm}_{1/18}\text{Ba}_{1/12}\text{PO}_3]_n$	0.1014	0.58	3496

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

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 $[\text{Na}_x\text{M}^{\text{III}}_{1-x/2a}\text{M}^{\text{III}}_{1-x/2a}\text{PO}_3]_n$ were found to be in the range ~ 3000. The chain length for these derivatives corresponding to ~ 30 units. The M_n values of these derivatives with $x = 3/4$ in the above composition were found to be in the range 2555 – 3070. The chain length for these derivatives correspondence to 25-30 units.

W= weight of the polymer sample used in titration

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

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 2500-3000, indicating a chain length equal to 25-30 units. These values are also in the same range as found in case of poly (alkaline earth – alkali metal phosphates) reported by Mehrotra & Oza¹³.

Viscosity studies:

The viscosity measurements of the complex polymetaphosphate derivatives of the composition: $[\text{Na}_x\text{M}^{\text{III}}_{1-x/2a}\text{M}^{\text{III}}_{1-x/2a}\text{PO}_3]_n$ 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)

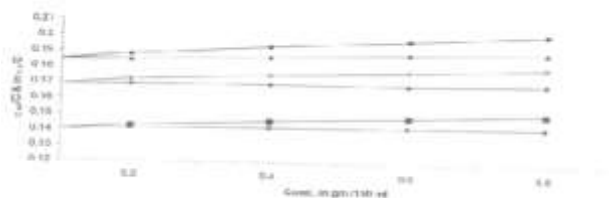


Figure 2: Plots of η_{sp}/C and $\ln \eta_r/C$ Vs Concentration

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 al¹⁴ for poly (ammonium/ amidium phosphates).

This type of behaviour is characteristic of linear polymer as suggested by Maron¹⁵ and Mead et. Al¹⁶.

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

S . N o .	Complex Polymetaphosphate	Concentration gm/100ml	η_{sp}/C	$\ln \eta_r/C$	F	G
1	$[Na_{3/4} Fe_{1/24} Mg_{1/16} PO_3]_n$	0.2	0.1197	0.1183	0.25	0.1496
		0.4	0.1244	0.1215	0.66	0.2073
		0.6	0.1296	0.1248	1.50	0.3240
		0.8	0.1348	0.1281	4.00	0.6740
2	$[Na_{3/4} Fe_{1/24} Zn_{1/16} PO_3]_n$	0.2	0.1511	0.1489	0.25	0.1888
		0.4	0.1533	0.1488	0.66	0.2555
		0.6	0.1558	0.1490	1.50	0.3895
		0.8	0.1585	0.1492	4.00	0.7925
3	$[Na_{3/4} Fe_{1/24} Ca_{1/16} PO_3]_n$	0.2	0.0934	0.0926	0.25	0.1168
		0.4	0.0968	0.0950	0.66	0.1614
		0.6	0.0998	0.0969	1.50	0.2495
		0.8	0.1029	0.0989	4.00	0.5147
4	$[Na_{3/4} La_{1/24} Mg_{1/16} PO_3]_n$	0.2	0.0890	0.0882	0.25	0.1120
		0.4	0.0911	0.0895	0.66	0.1519
		0.6	0.0936	0.0911	1.50	0.2342
		0.8	0.0962	0.0927	4.00	0.4814

5	[Na _{2/3} La _{1/18} Zn _{1/12} PO ₃] _n	0.2	0.115 4	0.114 2	0.25	0.144 2
		0.4	0.120 2	0.117 4	0.66	0.200 3
		0.6	0.125 9	0.121 4	1.50	0.314 7
		0.8	0.131 7	0.125 3	4.00	0.658 5
6	[Na _{2/3} Sm _{1/18} Ba _{1/12} PO ₃] _n	0.2	0.125 8	0.124 2	0.25	0.157 2
		0.4	0.128 7	0.125 6	0.66	0.214 5
		0.6	0.131 5	0.126 6	1.50	0.328 7
		0.8	0.134 4	0.127 7	4.00	0.672 0

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 polymers 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 al¹¹. The values of M_w obtained in this manner are given in table (4). The intrinsic viscosity (η) used in the above equation

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:

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

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 $X_m + X_M \lim_{C \rightarrow 0} [G] = G_n = 1.76 \times 10^{-5} \times M_w^*$ cannot 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 al¹⁷.

is replaced with the extrapolation of the linear transformation:

$$G=AF + B \tag{15}$$

where $Y = \eta_{sp}/C$, $X =$ concentration, $\alpha =$ 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'.

$$A = \frac{A-B}{\alpha} \quad \text{and} \quad b = B\alpha \tag{17}$$

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

1(18)



Figure 3: Plots of Factor G Vs F

Molecular weight distribution:

The ratio of M_w/M_n lies in the range 1.92-2.06 for these derivatives. Van-wazer¹⁸ and Newman¹⁹ 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 Flory²⁰, 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 al²¹ 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.

where the variables G & F are defined as:

$$G=Y/\alpha-X \ \& \ F=X/ \alpha-X \tag{16}$$

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:

$$X_m + X_M \lim_{C \rightarrow 0} [G] = G_n = 1.76 \times 10^{-5} \times M_w^* \tag{18}$$

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. The $[G_n]$ values can be used with more reliability for molecular weight determination of polyphosphate polymers.

S. No.	Complex Polymetaphosphates	M_n	M_w	M_n^*	M_w^*	M_w/M_n
1	$[Na_{3/4}Fe_{1/24}Mg_{1/16}PO_3]_n$	3242	6478	3239	6648	1.99
2	$[Na_{3/4}Fe_{1/24}Zn_{1/16}PO_3]_n$	4732	8410	4205	8466	1.77
3	$[Na_{3/4}Fe_{1/24}Ca_{1/16}PO_3]_n$	2585	5114	2556	5228	1.97
4	$[Na_{3/4}La_{1/24}Mg_{1/16}PO_3]_n$	2550	4887	2443	5057	1.91
5	$[Na_{2/3}La_{1/18}Zn_{1/12}PO_3]_n$	3160	6250	3125	6420	1.97
6	$[Na_{2/3}Sm_{1/18}Ba_{1/12}PO_3]_n$	3496	6989	3494	7103	1.99

Table 4: Number Average (M_n) & Weight Average Molecular Weight (M_w)

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:

$$X_m + X_M [G_n] = 3.52 \times 10^{-5} \times M_n^* \tag{19}$$

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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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