Synthesis and Characterization of Ternary (Bi-Bivalent) Polymetaphosphate Derivatives with Metachromatic studies

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ABSTRACT

Ternary (Bi-Bivalent) polymetaphosphate derivatives having the composition $[Na_xM^{II}_{1-x/2a}M'^{II}_{1-x/2a}PO_3]_n$, (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) have been synthesized by fusion technique. Metachromatic studies of ternary polymetaphosphate derivatives are carried out with some thiazene dyes like methylene blue and toludine blue. These metachromatic studies of ternary polymetaphosphate derivatives confirmed their long chain polymeric character.

Key words: Polymetaphosphate, Fusion technique, Metachromatic studies, Methylene Blue, Toludine Blue.

INTRODUCTION

The chemistry of phosphorous compounds has received considerable attention of a large number of research workers throughout the world during the last five decades. 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 polyphosphate consist of PO_4 tetrahedra sharing two of their oxygen atoms with adjoining PO_4 tetrahedra forming long chain polyanions of the formulation $(PO_3)_n^{-n}$. These polyanionic chains exhibit pronounced capacity for sequestration of metal ions.

In the present communication, ternary (Bi-Bivalent) polymetaphosphate derivatives of the composition:
$[Na_xM^{II}_{1-x/2a}M'^{II}_{1-x/2a}PO_3]_n$, (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) have been synthesized and long chain polymeric character of the above derivatives characterized by metachromatic studies have been recorded.

METACHROMATIC STUDIES

INTRODUCTION: Metachromatic reactions of ternary (bi-bivalent) complex polymetaphosphate derivatives with methylene blue (MB) and toludine blue (TB) have been studied. It has been found that the absorption maximum observed at 630 nm and 665 nm for TB and MB respectively are shifted to 530 nm and 580 nm in presence of complex polymetaphosphate derivatives. These shifts are similar to those reported in case of these dye solution in presence of Graham's salt as well as complex sodium and potassium polymetaphosphate derivatives. The metachromatic behaviour of complex polymetaphosphate derivatives is independent of their molecular weight and is exhibitive of their polyelectrolytic character.

Metachromacy is the variability of the colour of the dyes, produced by the addition of certain high molecular weight polyelectrolyte. The colour of the dyes produced in presence of polyelectrolyte is known as metachromatic colour. Such dyes are also known to disobey Beer's law deviation from which have been attributed to reversible polymerizations of dye molecules i.e. the polymer exhibits a colour different from the monomer.

Michaelis and Granick[1] have studied metachromacy of some thiazine dyes spectrophotometrically. The absorption maxima of the dye, according to these workers are shifted to lower wavelengths.Wiam[2] studied the metachromatic behaviour of sodium hexametaphosphate with toludine blue. It was observed that absorption maxima of aqueous solution of the dye are shifted to lower value i.e. 530 nm in presence of Graham's salt. Phosphates such as ortho-, pyro -, and tripoly- , other than polymetaphosphate derivatives do not produce metachromatic effect. Anne-Levine and Schubert[3] have also studied the metachromatic reaction of TB in presence of polyanion and suggested that the loose binding of the former with later is cause of metachromacy. Mckay and Hillson[4] studied the effect of different electrolytes in varying concentrations on the metachromatic behaviour of methylene blue. Mehrotra and Gupta[5] and later Mehrotra, Vyas and Ojha[6] have studied the metachromatic effect of complex polymetaphosphate derivatives of sodium, potassium, lithium and cesium on TB, MB and thionine dyes. Metachromacy produced by these derivatives was found to be similar to that of Graham's salt and indicative of their polyelectrolytic character.

These studies were used by these workers for elucidating the polymeric nature of the corresponding complex polymetaphosphates. The polymeric nature of $(BHPO_3)_n$ and complex polyphosphate of the composition $[BH_xM^{II}_{1-x/a}PO_3]_n$ was established by Vyas[7] and Mamta[8] by studying the metachromatic reactions of these derivatives towards cationic dyes. The above study was also considered useful for elucidating the long chain polymeric character of these complex polymetaphosphate derivatives of the composition:
$[Na_xM^{II}_{1-x/2a}M'^{II}_{1-x/2a}PO_3]_n$, (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).

MATERIAL AND METHODS

For preparation of ternary polymetaphosphate derivatives 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.

PREPARATION

Complex polymetaphosphate derivatives of the composition $[Na_xM^{II}_{1-x/2a}M'^{II}_{1-x/2a}PO_3]_n$, (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) were prepared by fusion technique in accordance with the equation given below:

When x=2/3

$$n\ 2/3\ NaH_2PO_4 + n\ 1/12\ M^{II}O + n\ 1/12 M'^{II}O + 1/3\ n\ NH_4H_2PO_4 \xrightarrow[\Delta]{900 \pm 25^{o}C} [Na_{2/3}M^{II}_{1/12}M'^{II}_{1/12}PO_3]_n + 1/3n\ NH_3 + 7/6\ n\ H_2O \quad (1)$$

When x=3/4

$$n\ 3/4\ NaH_2PO_4 + n\ 1/16\ M^{II}O + n\ 1/16\ M'^{II}O + 1/4\ n\ NH_4H_2PO_4 \xrightarrow[\Delta]{900 \pm 25^{o}C} [Na_{3/4}M^{II}_{1/16}M'^{II}_{1/16}PO_3]_n + 1/4\ n\ NH_3 + 9/8\ n\ H_2O \quad (2)$$

Method:

The reactants were taken in different molar ratio (keeping in view that M: P ratio equal to one) in a platinum crucible and mixed well with the help of a platinum stirrer. First it was heated at low temperature until the initial froathing due to vigorous evolution of ammonia, carbon dioxide and water vapour subsided. The temperature was then raised and the mixture heated till a melt was then put in a thermostatically controlled muffle furnace at 900 ± 25^{o}C for two hours. The products obtained in the form of a clear melt were immediately chilled between two stainless steel plates. The yield was almost theoretical and the composition was confirmed by estimating phosphorous and metal contents of the compounds.

Analysis of Phosphorous and Metals:

Phosphorous was estimated volumetrically as ammonium molybdate and metals by standard methods as described by Vogel[9] 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'^{II}	
		Exp	Cal.	Exp	Cal.	Exp	Cal.	Exp	Cal.
1	$[Na_{2/3}\ Mg_{1/12}Ba_{1/12}PO_3]_n$	28.70	28.75	14.17	14.21	1.79	1.87	10.58	10.61
2	$[Na_{2/3}\ Mg_{1/12}Ca_{1/12}PO_3]_n$	31.02	31.09	15.30	15.37	2.00	2.03	3.30	3.34
3	$[Na_{2/3}\ Mg_{1/12}Ni_{1/12}PO_3]_n$	30.58	30.62	15.11	15.13	1.88	2.00	4.78	4.83
4	$[Na_{2/3}\ Ba_{1/12}Ca_{1/12}PO_3]_n$	28.36	28.41	14.01	14.04	10.40	10.48	3.02	3.06
5	$[Na_{3/4}\ Ba_{1/16}Ca_{1/16}PO_3]_n$	28.66	28.88	16.01	16.06	7.89	7.99	2.30	2.33
6	$[Na_{3/4}\ Mg_{1/16}Ba_{1/16}PO_3]_n$	29.07	29.14	16.27	16.21	1.38	1.42	8.00	8.07
7	$[Na_{3/4}\ Mg_{1/16}Ca_{1/16}PO_3]_n$	30.20	30.91	17.10	17.19	1.48	1.51	2.42	2.49
8	$[Na_{3/4}\ Mg_{1/16}Zn_{1/16}PO_3]_n$	30.36	30.43	16.86	16.92	1.42	1.49	4.20	4.03
9	$[Na_{3/4}\ Ca_{1/16}Zn_{1/16}PO_3]_n$	30.04	30.14	16.72	16.76	2.38	2.40	2.90	3.99
10	$[Na_{3/4}\ Mg_{1/16}Ni_{1/16}PO_3]_n$	30.36	30.56	16.90	16.99	1.42	1.49	3.58	3.61
11	$[Na_{3/4}\ Ba_{1/16}Zn_{1/16}PO_3]_n$	28.33	28.46	15.78	15.83	7.82	7.88	3.72	3.77
12	$[Na_{3/4}\ Mg_{1/16}Cu_{1/16}PO_3]_n$	30.35	30.46	16.90	16.94	1.42	1.49	3.85	3.90
13	$[Na_{3/4}\ Zn_{1/16}Sr_{1/16}PO_3]_n$	27.72	27.78	15.40	15.46	3.62	3.68	4.85	4.91

Experimental:

Materials: Dyes: Methylene blue and Toludine blue have been employed for studying the metachromatic reactions. Both the dyes used in the study were of E. Merck grade. The dye samples were recrystallized from alcohol before use.

Polyelectrolyte: Polymetaphosphate of the composition $[Na_xM^{II}_{1-x/2a}M'^{II}_{1-x/2a}PO_3]_n$, (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) was used for these studies.

Solvent: Water was used as a solvent for the preparation of dye and polyelectrolyte solutions.

Method: The stock solutions were prepared by dissolving the weighed samples in double distilled water. The concentration of polyphosphate derivatives was taken in the range 0.2-1.0

$X10^{-3}$ M. The stock solutions of dyes were also prepared in similar manner. The final concentration of the dye in the dye – polymer solution was maintained at a fixed value which is 1.6 $X10^{-4}$ M for TB and 3.2 X 10^{-5} M for MB. A lower concentration of MB was preferred because at higher concentration the particles of MB settled down on keeping the solution for some time after the addition of complex polymetaphosphate derivatives.

Measurements: The optical densities of the dyes (MB or TB) alone and in presence of polyphosphate were measured with the help of **UV- Visible Spectrophotometer (Model - 301E)**. The conductometric titrations of dyes were carried out by employing digital conductivity bridge (Model – CC 601) and a conductivity cell having cell factor 0.90. The titrations were performed by drop wise addition of 2 $X10^{-2}$ M solution of polymer to the 25 ml solution of 1.0 X 10^{-3} M dye in a 50 ml beaker. The solution mixtures were stirred vigorously and allowed to stand for some time to attain equilibrium before measuring the conductance.

Result and Discussions

The absorption spectra of the aqueous solution of MB and TB were recorded in the absence and presence of complex polymetaphosphate derivative of the composition $[Na_xM^{II}_{1-x/2a}M'^{II}_{1-x/2a}PO_3]_n$, (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). There representative spectra are given in figure 1 to 4. The position of the main band (α) and metachromatic band (β) observed in the case of dye solution alone and in the presence of polyphosphate derivatives recorded in table 1 to 4.

Table 1: Absorbance of the aqueous solution of Methylene Blue (3.2 X 10^{-5} M)

Sr. No.	Wave Length (λ) (nm)	Absorbance
1	400	0.03
2	420	0.04
3	440	0.05
4	460	0.07
5	480	0.08
6	500	0.10
7	520	0.11
8	540	0.14
9	560	0.25
10	580	0.44
11	600	0.68
12	620	1.0
13	640	1.26
14	660	1.53
15	665	1.61
16	670	1.51
17	680	1.09
18	700	0.36
19	720	0.21
20	740	0.16
21	760	0.14
22	780	0.12
23	800	0.10

Table 2: Absorbance of the aqueous solution of Toludine Blue (1.6 X 10^{-4} M)

Sr. No.	Wave Length (λ) (nm)	Absorbance
1	400	0.06
2	420	0.07
3	440	0.09
4	460	0.11
5	480	0.13
6	500	0.17
7	520	0.21
8	540	0.33
9	560	0.54
10	580	0.77
11	600	1.11
12	620	1.51
13	630	1.65
14	640	1.46
15	660	1.16
16	680	0.92
17	700	0.71
18	720	0.53
19	740	0.42
20	760	0.31
21	780	0.26
22	800	0.22

Table 3: Absorbance of main band (α) and metachromatic band (β) of the aqueous solution of methylene blue (3.2 X 10^{-5} M) in the presence of complex polymetaphosphate derivatives

S. N	COMPLEX POLYMETAPHOSPHATE	CONCENTRATION									
		0.2 X 10^{-3}M		0.4 X 10^{-3}M		0.6 X 10^{-3}M		0.8 X 10^{-3}M		1.0 X 10^{-3}M	
		A	B	A	B	α	B	A	B	A	B
1	$[Na_{2/3} Mg_{1/12}Ba_{1/12}PO_3]_n$	0.270	0.665	0.276	0.658	0.220	0.634	0.265	0.642	0.258	0.652
2	$[Na_{2/3} Mg_{1/12}Ca_{1/12}PO_3]_n$	0.302	0.643	0.298	0.656	0.266	0.609	0.275	0.634	0.292	0.657
3	$[Na_{3/4} Mg_{1/16}Ba_{1/16}PO_3]_n$	0.294	0.610	0.276	0.625	0.285	0.636	0.280	0.644	0.302	0.650
4	$[Na_{3/4} Mg_{1/16}Ca_{1/16}PO_3]_n$	0.298	0.610	0.282	0.625	0.276	0.632	0.294	0.642	0.302	0.653
5	$[Na_{3/4} Mg_{1/16}Zn_{1/16}PO_3]_n$	0.302	0.612	0.282	0.629	0.274	0.634	0.285	0.642	0.296	0.649

6	$[Na_{3/4}\ Ca_{1/16}Zn_{1/16}PO_3]_n$	0.295	0.678	0.302	0.688	0.278	0.649	0.310	0.683	0.316	0.693
7	$[Na_{3/4}\ Mg_{1/16}Ni_{1/16}PO_3]_n$	0.262	0.666	0.275	0.672	0.278	0.654	0.274	0.656	0.296	0.662
8	$[Na_{3/4}\ Ba_{1/16}Zn_{1/16}PO_3]_n$	0.332	0.628	0.287	0.654	0.264	0.628	0.280	0.672	0.296	0.648
9	$[Na_{3/4}\ Ba_{1/16}Ca_{1/16}PO_3]_n$	0.265	0.668	0.274	0.675	0.262	0.652	0.270	0.654	0.296	0.664

Table 4: Absorbance of main band (α) and metachromatic band (β) of the aqueous solution of toludine blue (1.6 X 10^{-5} M) in the presence of complex polymetaphosphate derivatives

S. N	COMPLEX POLYMETAPHOSPHATE	CONCENTRATION									
		0.2 X 10^{-3}M		0.4 X 10^{-3}M		0.6 X 10^{-3}M		0.8 X 10^{-3}M		1.0 X 10^{-3}M	
		α	B	A	B	α	B	α	B	A	B
1	$[Na_{2/3}\ Mg_{1/12}Ba_{1/12}PO_3]_n$	0.648	1.184	0.655	1.168	0.624	1.156	0.682	1.174	0.676	1.145
2	$[Na_{2/3}\ Mg_{1/12}Ca_{1/12}PO_3]_n$	0.630	1.128	0.654	1.122	0.618	1.166	0.675	1.175	0.662	1.148
3	$[Na_{3/4}\ Mg_{1/16}Ba_{1/16}PO_3]_n$	0.624	1.125	0.635	1.114	0.650	1.119	0.672	1.167	0.646	1.178
4	$[Na_{3/4}\ Mg_{1/16}Ca_{1/16}PO_3]_n$	0.628	1.124	0.634	1.127	0.615	1.112	0.657	1.146	0.662	1.151
5	$[Na_{3/4}\ Mg_{1/16}Zn_{1/16}PO_3]_n$	0.616	1.121	0.632	1.123	0.638	1.119	0.665	1.148	0.646	1.151
6	$[Na_{3/4}\ Ca_{1/16}Zn_{1/16}PO_3]_n$	0.725	1.114	0.710	1.131	0.672	1.106	0.646	1.098	0.654	1.143
7	$[Na_{3/4}\ Mg_{1/16}Ni_{1/16}PO_3]_n$	0.628	1.072	0.675	1.176	0.654	1.152	0.642	0.978	0.636	0.985
8	$[Na_{3/4}\ Ba_{1/16}Zn_{1/16}PO_3]_n$	0.610	1.132	0.628	1.122	0.615	1.154	0.634	1.195	0.620	1.184
9	$[Na_{3/4}\ Ba_{1/16}Ca_{1/16}PO_3]_n$	0.654	0.987	0.635	0.978	0.620	1.075	0.688	1.175	0.646	1.151

It can be seen from the figures and data's that the main band (α) observed at 630 & 665nm for TB and MB respectively are shifted to 530 and 580nm in presence of complex polymetaphosphate derivatives. These shifts are similar to those reported in case of these dye solution in presence of Graham's salt as well as for complex sodium and potassium phosphate derivatives. It confirms that complex polymetaphosphate derivatives possess polymeric character similar to Graham's salt. It is also evident from these studies that polyanion induced metachromacy of these dyes is very much dependent on the concentration of polyphosphate.

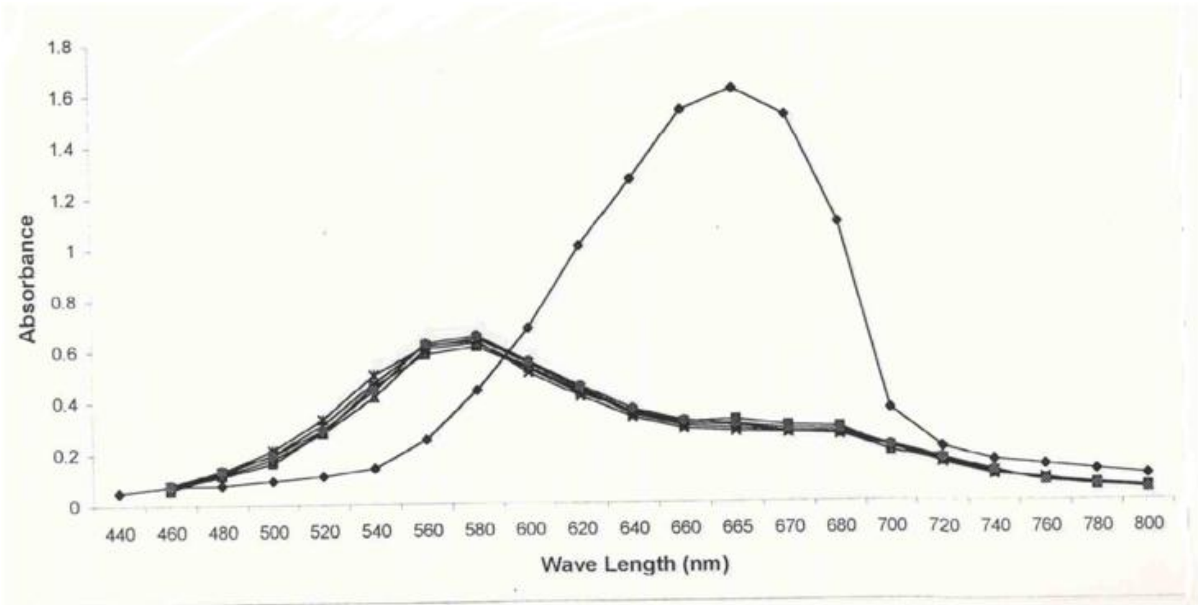

Figure 1: Absorption spectra of aqueous solution of Methylene blue (3.2 X 10^{-5}) alone and in presence of the varying concentration of complex polymetaphosphate $[Na_{3/4}Mg_{1/16}Ca_{1/16}PO_3]_n$

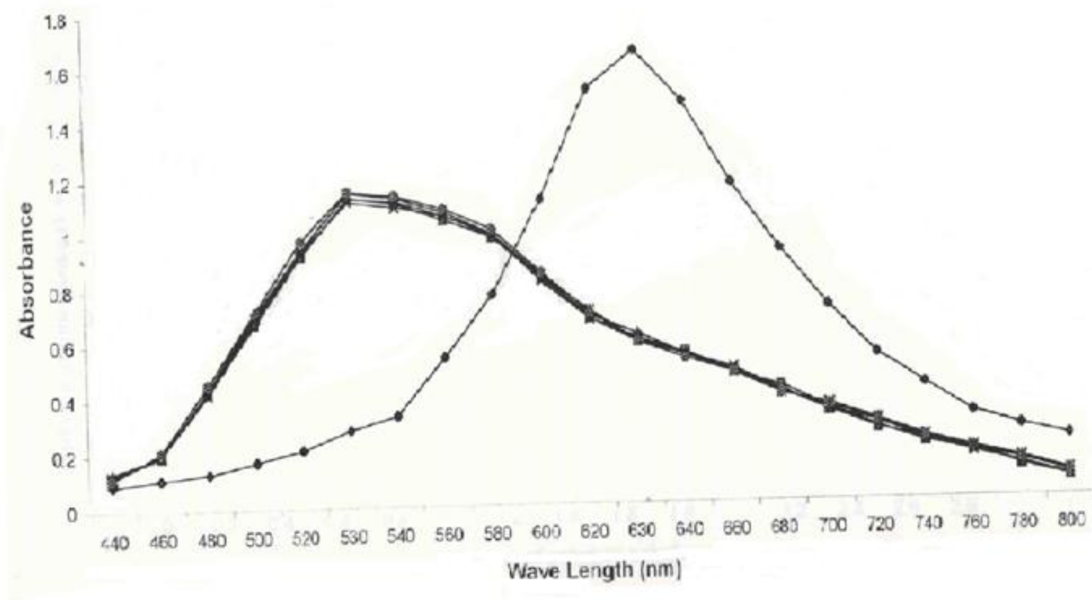

Figure 2: Absorption spectra of aqueous solution of Toludine Blue (1.6X10^{-4} M) alone and in presence of the varying concentration of complex polymetaphosphate $[Na_{3/4}Mg_{1/16}Ca_{1/16}PO_3]_n$

The term metachromacy (R) can be defined as follows:

$$R = \frac{\text{Absorbance at metachromatic band } (\beta)}{\text{Absorbance at main band } (\alpha)}$$

The metachromatic values for these dyes at varying concentration of polymetaphosphates have been recorded in table 5 to 6

Table 5: Metachromacy $\left(\frac{\text{Absorbance at metachromatic band } (\beta)}{\text{Absorbance at main band } (\alpha)}\right)$ of aqueous solution of Methylene blue ($3.2X10^{-5}$ M) at different P/D ratio.

Sr. No.	Complex Polymetaphosphate	Metachromacy				
		P/D Ratio				
		6.25	12.50	18.75	25.00	31.25
1	$[Na_{2/3}Mg_{1/12}Ba_{1/12}PO_3]_n$	2.46	2.38	2.88	2.42	2.52
2	$[Na_{2/3}Mg_{1/12}Ca_{1/12}PO_3]_n$	2.12	2.20	2.28	2.30	2.25
3	$[Na_{3/4}Mg_{1/16}Ba_{1/16}PO_3]_n$	2.07	2.26	2.23	2.30	2.15
4	$[Na_{3/4}Mg_{1/16}Ca_{1/16}PO_3]_n$	2.04	2.21	2.28	2.18	2.16
5	$[Na_{3/4}Mg_{1/16}Zn_{1/16}PO_3]_n$	2.02	2.23	2.31	2.25	2.19
6	$[Na_{3/4}Ca_{1/16}Zn_{1/16}PO_3]_n$	2.29	2.27	2.33	2.20	2.19
7	$[Na_{3/4}Mg_{1/16}Ni_{1/16}PO_3]_n$	2.54	2.44	2.35	2.39	2.23
8	$[Na_{3/4}Ba_{1/16}Zn_{1/16}PO_3]_n$	1.87	2.27	2.37	2.40	2.18
9	$[Na_{3/4}Ba_{1/16}Ca_{1/16}PO_3]_n$	2.52	2.46	2.48	2.42	2.24

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Table 6: Metachromacy $\left(\frac{\text{Absorbance at metachromatic band } (\beta)}{\text{Absorbance at main band } (\alpha)}\right)$ of aqueous solution of Toludine blue ($1.6X10^{-4}$ M) at different P/D ratio.

Sr. No.	Complex Polymetaphosphate	Metachromacy				
		P/D Ratio				
		6.25	12.50	18.75	25.00	31.25
1	$[Na_{2/3}Mg_{1/12}Ba_{1/12}PO_3]_n$	1.82	1.78	1.85	1.72	1.69
2	$[Na_{2/3}Mg_{1/12}Ca_{1/12}PO_3]_n$	1.79	1.71	1.88	1.74	1.73
3	$[Na_{3/4}Mg_{1/16}Ba_{1/16}PO_3]_n$	1.80	1.75	1.72	1.73	1.82
4	$[Na_{3/4}Mg_{1/16}Ca_{1/16}PO_3]_n$	1.78	1.77	1.80	1.74	1.73
5	$[Na_{3/4}Mg_{1/16}Zn_{1/16}PO_3]_n$	1.81	1.77	1.75	1.72	1.78
6	$[Na_{3/4}Ca_{1/16}Zn_{1/16}PO_3]_n$	1.53	1.59	1.64	1.69	1.74
7	$[Na_{3/4}Mg_{1/16}Ni_{1/16}PO_3]_n$	1.70	1.74	1.76	1.52	1.54

8	$[Na_{3/4}Ba_{1/16}Zn_{1/16}PO_3]_n$	1.85	1.78	1.87	1.88	1.90
9	$[Na_{3/4}Ba_{1/16}Ca_{1/16}PO_3]_n$	1.50	1.54	1.73	1.70	1.78

From these data following conclusion can be drawn:

1 The values of metachromacy (R) for these dyes are independent of the molecular weight or chain length of the complex polymetaphosphates derivatives.
2 Maximum metachromatic values (R) are obtained at P/ D ratio equal to 12.5 and 25.00 for MB and TB respectively.

Krishnan and Coworkers[10] have also found that metachromacy of TB is independent of the molecular weight of sodium polymetaphosphates. This type of behavior was further confirmed by Mehrotra and Gupta[11]. A P/D ratio equal to 5 is observed for TB in presence of polyphosphates. Although Wiame has determined a P/D ratio equal to 8 for solution of TB in presence of sodium hexametaphosphate. This difference occurs because of difference in experimental conditions. For MB a P/D ratio equal to 12.5 is observed in presence of polyphosphates. However a critical range of P/D ratio, necessary for inducing metachromacy in MB has not been reported so far.

Stiochiometry of dye – polymer complex:

The dye ion association with polyanion was investigated conductometrically[12-16] . Figure 3 to 4 show the conductometric titration curves drawn on the basis of specific conductance data given in the conductometric titration curves at 1:1 molar ratio of dye and polymer in solution given in table 7 and table 8. This indicate that MB and TB can site-bound to a complex polyphosphate at 1:1 molar ratio irrespective of the chain length with phosphate residue of the polymer. Similar results were obtained by Yamaoka et al[17] for a reaction between crystal violet and Graham's salt on the basis of conductometric studies. Further Pal et al[12-13] established that polyanions such as ATP, $HgCl_2$, KI etc. form a complex with methylene blue.

Table 7: Specific conductance (k X 10^{-4}) of 25 ml aqueous solution of methylene blue (1.0 X 10^{-4}M) in presence of varying concentration of complex polymetaphosphate

Volume of polymer solution (ml)	Specific conductance (k X10^{-4} M) in Ω^{-1} cm^{-1}					
	I	II	III	IV	V	VI
0.00	.129	.138	.162	.158	.173	.145
0.20	.131	.140	.165	.162	.176	.150
0.40	.133	.142	.168	.164	.178	.154
0.60	.135	.144	.170	.166	.182	.156
0.80	.137	.146	.176	.170	.186	.158
1.00	.140	.150	.182	.174	.190	.162
1.20	.146	.154	.187	.177	.197	.167
1.40	.153	.162	.190	.185	.204	.172
1.60	.166	.175	.196	.192	.208	.184
1.80	.187	.192	.224	.212	.232	.200
2.00	.206	.215	.247	.236	.257	.226

2.20	.233	.240	.272	.262	.284	.252
2.40	.258	.266	.290	.287	.303	.276
2.60	.276	.288	.318	.306	.326	.297
2.80	.302	.310	.342	.331	.352	.322
3.00	.333	.332	.364	.354	.376	.343

I=$[Na_{2/3}\ Mg_{1/12}Ni_{1/12}PO_3]_n$ II=$[Na_{2/3}Ba_{1/12}Ca_{1/12}PO_3]_n$
III=$[Na_{3/4}Ba_{1/16}Ca_{1/16}PO_3]_n$ V = $[Na_{3/4}\ Mg_{1/16}Ba_{1/16}PO_3]_n$ V = $[Na_{3/4}\ Mg_{1/16}Ca_{1/16}PO_3]_n$ VI = $[Na_{3/4}\ Mg_{1/16}Zn_{1/16}PO_3]_n$
C = Concentration of polyphosphate solution (2 X 10^{-3} F)

Table 8: Specific conductance (k X 10^{-4}) of 25 ml aqueous solution of toludine blue (1.0 X 10^{-4}M) in presence of varying concentration of complex polymetaphosphate

Volume of polymer solution (ml)	Specific conductance (k X10^{-4} M) in Ω^{-1} cm^{-1}					
	I	II	III	IV	V	VI
0.00	.410	.392	.380	.431	.361	.450
0.20	.413	.394	.382	.433	.363	.452
0.40	.417	.396	.384	.435	.365	.454
0.60	.419	.398	.386	.438	.367	.456
0.80	.421	.403	.389	.443	.369	.458
1.00	.423	.405	.393	.445	.372	.463
1.20	.425	.407	.395	.447	.374	.467
1.40	.428	.409	.397	.454	.376	.475
1.60	.436	.415	.404	.458	.379	.486
1.80	.444	.427	.406	.466	.383	.493
2.00	.462	.443	.425	.485	.395	.505
2.20	.507	.486	.448	.526	.416	.548
2.40	.544	.522	.483	.567	.448	.586
2.60	.573	.564	.537	.595	.505	.628
2.80	.615	.596	.578	.638	.549	.654
3.00	.658	.634	.615	.676	.586	.692

I=$[Na_{2/3}\ Mg_{1/12}Ni_{1/12}PO_3]_n$ II=$[Na_{2/3}Ba_{1/12}Ca_{1/12}PO_3]_n$
III=$[Na_{3/4}Ba_{1/16}Ca_{1/16}PO_3]_n$ V = $[Na_{3/4}\ Mg_{1/16}Ba_{1/16}PO_3]_n$ V = $[Na_{3/4}\ Mg_{1/16}Ca_{1/16}PO_3]_n$ VI = $[Na_{3/4}\ Mg_{1/16}Zn_{1/16}PO_3]_n$
C = Concentration of polyphosphate solution (2 X 10^{-3} F)

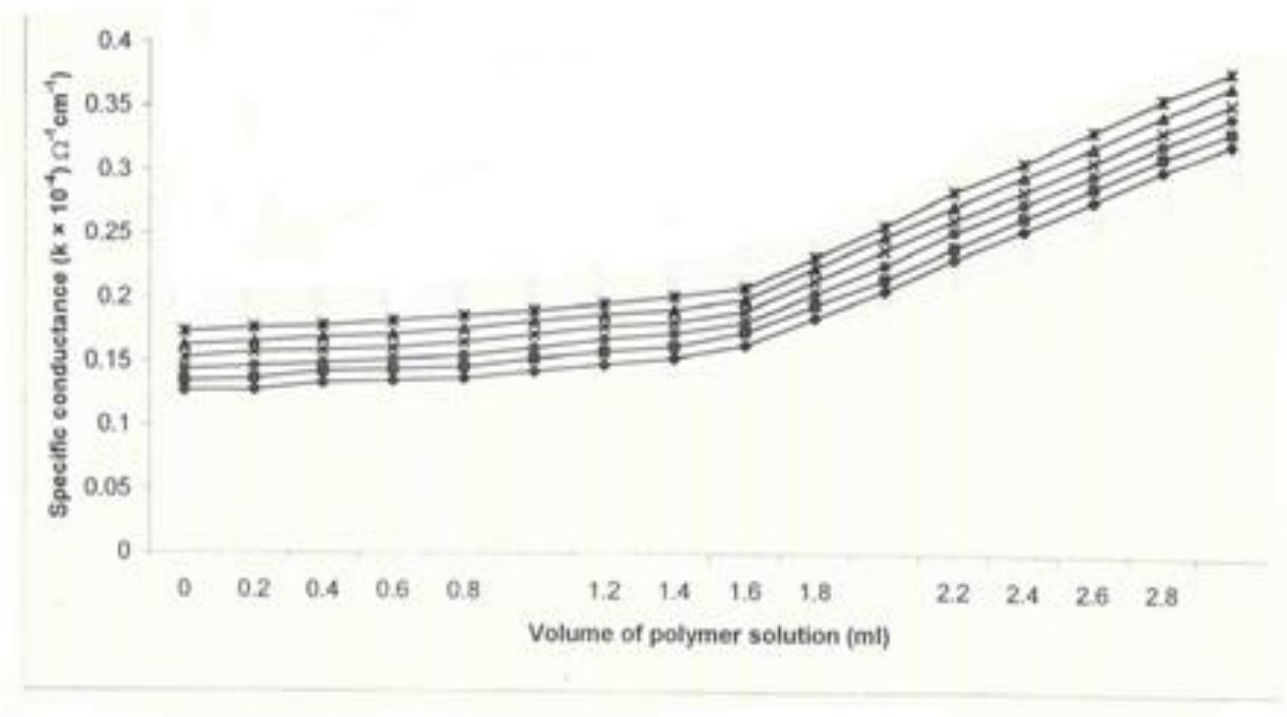

Figure 3 : Specific Conductance (k X 10^{-4}) of 25ml of aqueous solution of MB (1 X 10^{-4}) in presence of varying concentration of complex polymetaphosphates

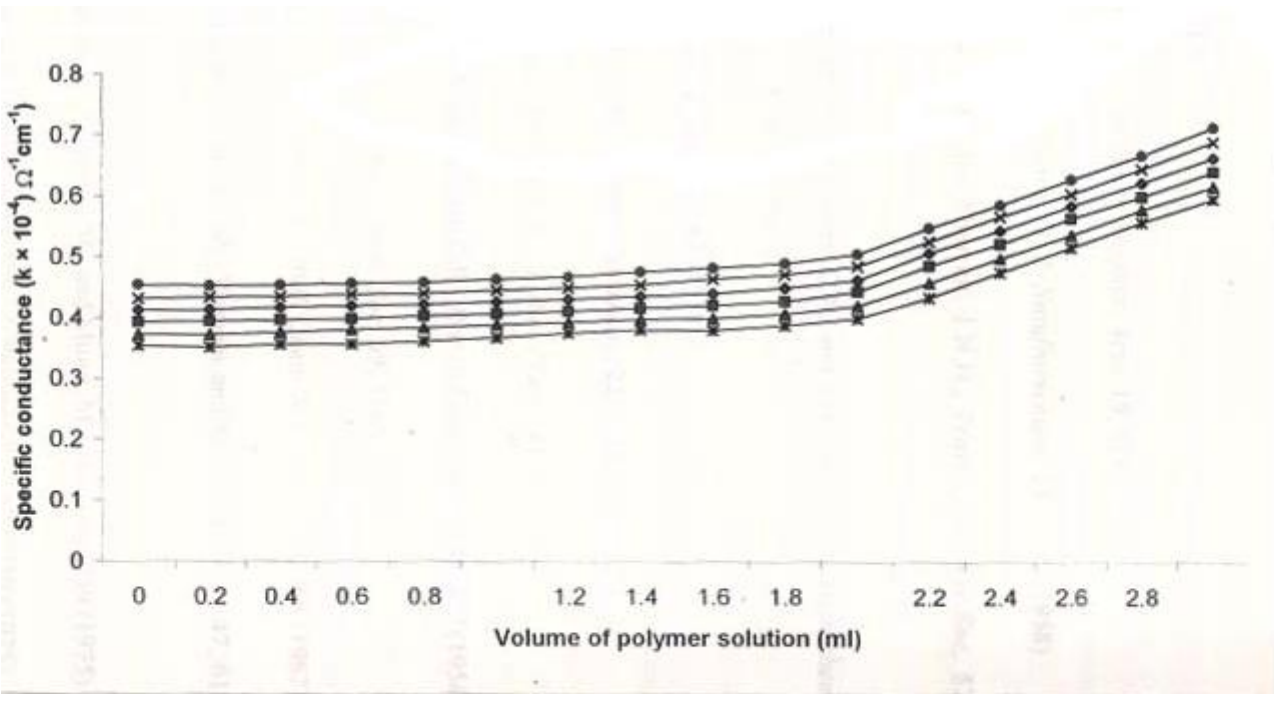

Figure 4: Specific Conductance (k X 10^{-4}) of 25ml of aqueous solution of TB (1 X 10^{-4}) in presence of varying concentration of complex polymetaphosphates

The observation of inflection in the conductometric titration curves of dye and polymer at 1:1 molar ratio irrespective of chain length of polyphosphates, indicate that metachromacy of dye polymer is enhanced due to their site binding with polymer chains of polyelectrolytes like complex polyphosphate derivatives.

Scheibe[18] and Robinowitch[19] attributed deviations (even at very low concentration) from Beer's law in the Spectrophotometric studies of aqueous solution of MB and TO to the formation of dimeric cations $(MB)^{+2}$ and $(TO)^{+2}$ respectively.

The metachromatic behaviour of thiazine dyes in presence of agar – agar has been attributed to the increased polymerization of dye molecules by Michaelis and Granick[1]. According to Walton and Rickett[20] in the case of sulfonated dextranes, the reactive groups on dextrane are responsible for the metachromatic behaviour, which can be attributed to polymerization of the dye molecules. However Levine and Schubert[3] have explained the metachromatic behaviour of dye molecule is due to loose site bonding with the polyanions.

In view of these observations the metachromatic behaviour of MB and TB in presence of polyphosphate derivatives can be attributed to increased polymerizations and counter ion associations with dye cations. The association of dye ions with polyphosphate chain can be explained by considering an ion – exchange reaction stated below:

$$Y(D)_2^{++} + [Na_x\, M^{II}_{1\text{-}x/2a}\, M'^{II}_{1\text{-}x/2a}\, PO_3]_n. \rightarrow [\, Na_{x\text{-}2y}\, D_{2y} M^{II}_{1\text{-}x/2a} M'^{II}_{1\text{-}x/2a} PO_3]_n + n2YNa^+$$

where D = MB or TB, (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).

The dye ions are highly polarisable in comparison to cations and can be exchanged with the later on the polyanion. The most plausible explanation of the metachromatic effect of polyelctrolytes seems to be that the dye cations assume a more symmetrical conformation in aqueous solution while associating with the polymer chain and the system absorb at lower wave length.

Conclusion:

The important conclusion of the above study to us is that these metachromatic reactions are the best evidence of chain like character of the complex plymetaphosphate derivatives and a similar behaviour to that of Graham's salt.

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