

Characterization of some Organic Poly(aminiumphosphate)s. Part B. Metachromatic Reactions and Paper Chromatographic Studies

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SUMMARY

Metachromatic reactions of MB and AO are studied with poly(aminium phosphate)s. The main band (α) at 665 m μ and 492 m μ for MB and AO are shifted to 580 m μ and 455 m μ respectively (β -bands). The metachromatic values at different concentrations of poly(aminium phosphate)s are also reported. The dye association for MB with these polymer derivatives is investigated conductometrically as well. It is observed that MB can be at the most bind with the phosphate residue of polymer upto 1:1 molar ratio. The polymeric nature was further established by paper chromatographic technique in Terry's, Ebel's & Pfrengle's solvents.

INTRODUCTION

In the previous paper (VYAS et al. 1979) we described the molecular weights and conductance studies of some organo poly(aminium phosphate)s. In the present communication we have used paper chromatographic studies and metachromatic reactions in order to ascertain their polymeric nature.

METACHROMATIC REACTIONS

Methylene Blue (MB) and Acridine Orange (AO) used in these reactions were purified twice with water and dried to obtain completely anhydrous sample. The stock solutions of dye were prepared in double distilled water. The final concentration of dye was kept at 3.2×10^{-4} M for MB and 4.0×10^{-5} M for AO. The concentration of polymer, in dye solution, was in the range of 0.2 to 1.2×10^{-3} M. The absorption spectra were recorded with the help of a Toshniwal spectrophotometer after equilibrating the solutions for about half an hour.

Paper chromatograms were run in Terry's solvent [chloroacetic acid, isopropanol, acetone, water and 0.25% EDTA in concentrated NH_4OH , 50 gm: 250 ml: 350 ml: 300 ml: 100 ml: 15 ml .], Ebel's solvent (tert.butyl alcohol, water and formic acid, 80:20:5 ml) and Pfrengle's solvent [60 ml of methanol : 10.3 ml of trichloroacetic acid (100 gm TCAA in 500 ml of water and 22.7 ml of ammonia) : 5 ml acetic acid (20 ml acid in 80 ml water) : 12.5 ml water]. An ascending technique was employed for evaluating the R_f and R_g values for various polymer derivatives.

$$\text{where } R_f = \frac{\text{Distance Travelled by solute}}{\text{Distance Travelled by solvent}}$$

$$R_g = \frac{\text{Distance Travelled by phosphate under study}}{\text{Distance Travelled by orthophosphate}}$$

RESULTS AND DISCUSSION

From the spectral changes observed in case of methylene blue (MB) and acridine orange (AO) in the presence of poly(aminium phosphate)s, it was observed that the main bands (α -band) at 665 m μ and 492 m μ for MB and AO are shifted to 580 m μ and 455 m μ respectively (β -bands) Fig. A & B. The position of bands corresponds nearly to the same wave-lengths as reported in case of these dye solutions in presence of Graham's salt (LEVINE et al. 1952) as well as complex sodium- and potassium polyphosphate derivatives (MEHROTRA et al. 1970). It has also been reported that except high polymer derivatives of phosphates (WIAME 1947) none of the other salts, such as ortho-, pyro- and tripolyphosphates are able to induce metachromasy in dye solutions. It confirms that poly(aminium phosphate)s possess polymeric character similar to that of the Graham's salt.

The metachromatic ratio, (R)

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

for these dyes at varying concentrations of polyphosphate has been recorded in Table-1.

Table-1 : Metachromatic values(R) for various poly(amminium phosphate)s.

Substance	Concentrations(C x 10 ⁻³ M)				
	0.2	0.4	0.6	0.8	1.0
1.a	2.56* (2.13)+	2.68 (2.19)	2.59 (2.44)	2.54 (2.22)	2.45 (2.02)
1.b	1.66 (1.83)	2.20 (1.80)	2.11 (1.97)	2.09 (1.65)	1.94 (1.60)
1.c	1.50 (1.49)	1.90 (1.75)	1.65 (1.85)	1.57 (1.63)	1.50 (1.59)
1.d	3.10 (2.10)	3.30 (2.20)	3.20 (2.28)	2.90 (1.90)	2.80 (1.85)
1.e	2.78 (2.40)	2.87 (2.38)	2.80 (2.48)	2.65 (2.40)	2.60 (2.35)
1.f	2.54 (2.33)	2.69 (2.37)	2.60 (2.48)	2.50 (2.33)	2.48 (2.28)
II	1.48 (1.92)	2.08 (1.99)	1.90 (2.09)	1.80 (2.00)	1.75 (1.92)

* R values for MB

+ R values for AO

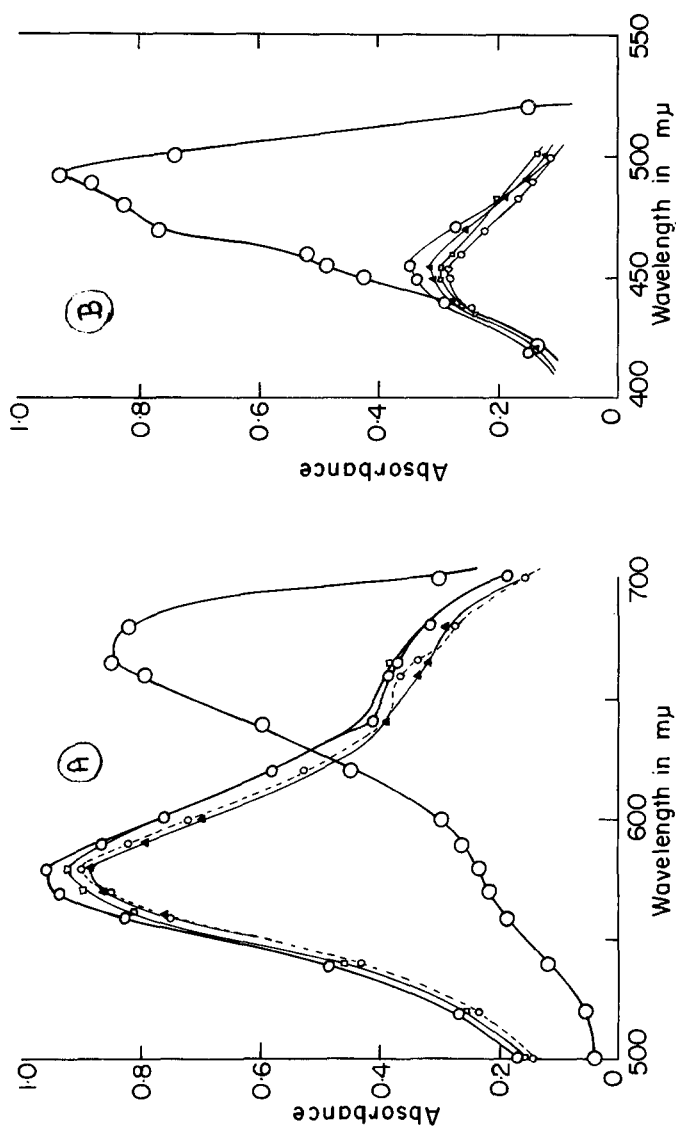


Fig. Absorption spectra of aqueous solution of methylene blue [$3.2 \times 10^{-4} M$], A, and acridine orange [$4.0 \times 10^{-5} M$], B, in presence of various concentration [$C \times 10^{-3} M$], [O-O-O, \circ -0.2, \blacktriangle -0.4, \circ -0.6 and \square -1.0] of $[(CH_2)_3C NH_3 PO_3]_n$

* Only metachromatic values (R) are reported for remaining polymer derivatives.
(See table 1)

From the table it is revealed that maximum metachromatic values are obtained at poly-phosphate concentrations of $0.4 \times 10^{-3}M$ and $0.6 \times 10^{-3}M$ in case of MB and AO respectively. From these data it can be inferred that a maximum metachromatic value is obtained at different P/D (phosphate/dye) ratio for different dyes. In case of AO the maximum metachromasy is observed at P/D equal to 15 in presence of these poly(aminium phosphate)s. MIURA et al.(1967) have pointed out that maximum P/D ratio equal to 3 and 6 is necessary for inducing metachromasy in presence of poly(sodium phosphate)s. Recently YAMAOKA et al. (1974) showed a relationship between chain length of phosphate derivatives and metachromasy. They observed that maximum metachromasy is obtained at P/D ratio of 3 and 30 with the chain length in the range of 7-20. In another publication the same authors (YAMAOKA et al. 1975) have shown that no metachromasy was observed in samples with chain length lesser than seven. However, no definite trend is observed for metachromatic values and the molecular weights of these poly(aminium phosphate)s. KRISHNAN et al.(1954) have also found that metachromatic behaviour of toluidine blue(TB) is independent of the molecular weights. This type of behaviour was further confirmed by MEHROTRA et al. (1964) as well. Hence, on the basis of studies reported it can be concluded that poly(aminium phosphate)s are polymeric in nature similar to Graham's salt and alkali polymetaphosphates.

The dye ion association (MB) with poly anion was investigated conductometrically(YAMAOKA et al. 1974). A sharp inflection is observed in the conductometric titration curves (Fig. C) at 1:1 molar ratio of dye with polymer solution. The inflections are observed at 1:1 mole ratio irrespective of chain length of poly(aminium phosphate)s. It indicates that MB can at the most bind with the phosphate residue of the polymer upto 1:1 molar ratio. These observations are in accordance with the studies on interaction of cationic dyes with polyphosphates reported by Yamaoka and later on by PAL et al.(1971, 1973).

The R_f and R_g values of these poly(aminium phosphate)s are measured in Terry's, Ebel's and Pfrengle's solvents respectively. The polymeric nature of these derivatives is indicated from the straight line plot of R_g values versus negative log of chain length (\bar{n}_C) of these derivatives (Fig. D). From the plots it is evident that the R_g values of these polymeric derivatives varies with the degree of polymerization.

From the figure it is evident that Terry's solvent (TERRY et al. 1973) gives higher R_g values for polyphosphate anions in lesser time(15 \bar{n}) whereas two other solvents mentioned above requires longer running times; 24h for Ebel's solvent and 26h for Pfrengle's solvent. Secondly no appreciable trailing of spots was observed in Terry's solvent. It

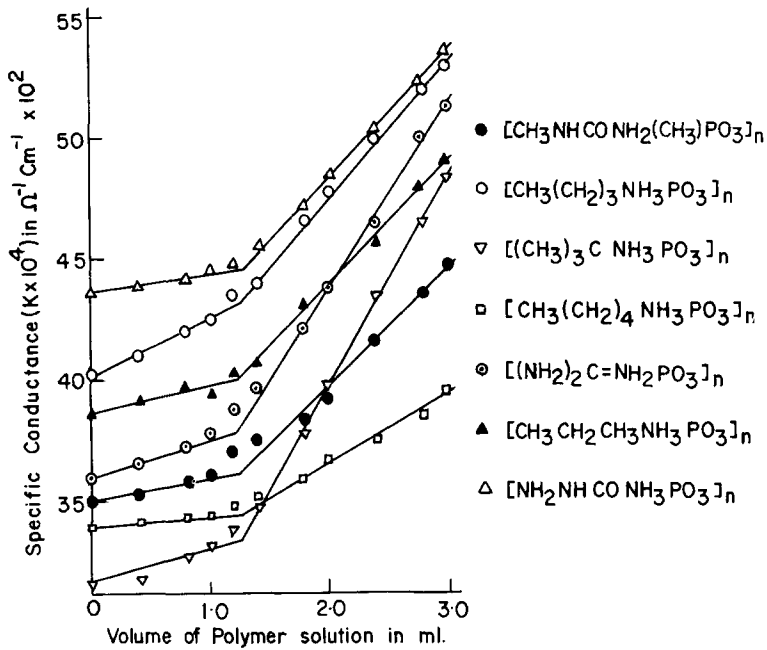
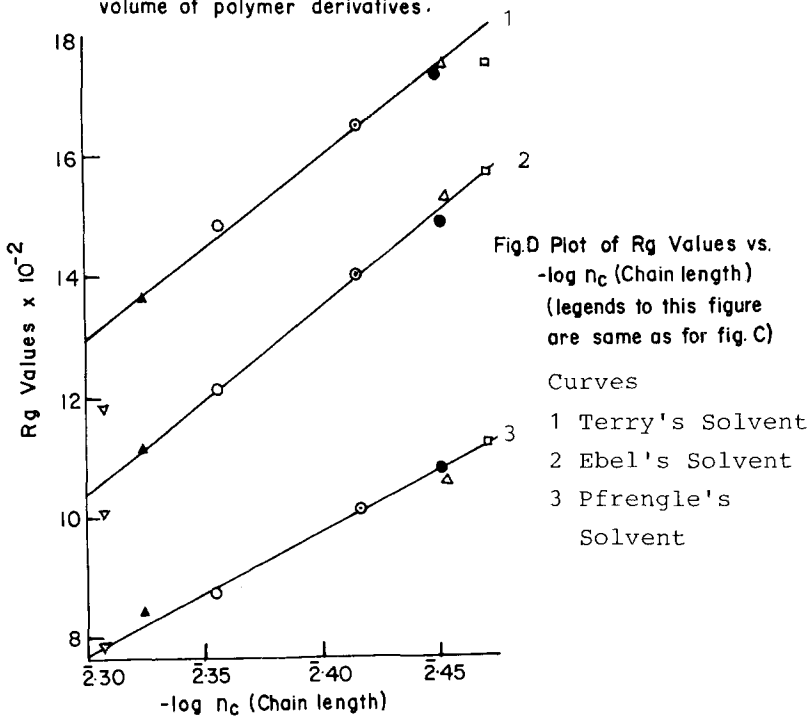


Fig.C Plot of specific conductance versus volume of polymer derivatives.



may be attributed to the differences in mobility of these solvents. All these solvents are acidic in nature, but differ in their viscosities. Ebel's solvent is composed of a large excess of tert.butyl alcohol which makes it less mobile as compared to Terry's solvent which has acetone, isopropanol and water as the major constituents. Pfrengle's solvent on the other hand consists of methanol as a major constituent and contains less water due to which its mobility is also lower in comparison to Terry's solvent.

Chromatograms of these derivatives also show two spots of very weak intensity along with those of the polyphosphate. The R_f values of these spots corresponds to ortho- and trimetaphosphates. These spots are probably due to initial hydrolysis of polyphosphate chain in aqueous solution which has been considered to be less than 2-2.5% (THILO et al.1957, 1961).

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