Molecular Weights and Conductance Studies of Some Organic Poly(aminiumphosphate)s

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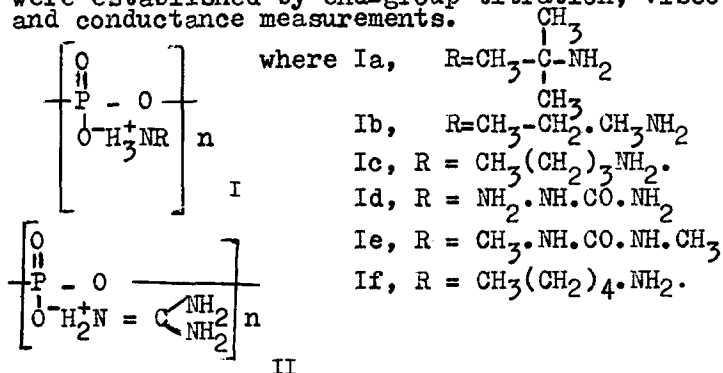Department of Chemistry, University of Rajasthan Jaipur, India

Summary

Long chain poly(aminiumphosphate)s of general composition $(BHPO_3)_n$ (where BH = organic cations) were prepared by precipitation technique. The composition was established by the analysis of these derivatives for N and P. The polymeric nature was confirmed by their molecular weight determinations by end group titration and viscosity methods. Conductance studies at different concentrations confirmed their polyelectrolytic behaviour.

Introduction

Polyphosphates are the important group of inorganic polymers exhibiting a high degree of hydrolytic stability in aqueous solution and thermal stability in solid state. The chemistry of ammonium polyphosphates have been investigated by several workers(CHOUGHULEY et al, OKAZAKI et al. 1974). However, a systematic study of organoaminium polyphosphates have not been undertaken so far. Guanidine, an analogue of urea, have been used for the purification of tetra phosphate (QUIMBY, KRAUSE, 1957). A large decrease in pH by the addition of guanidine to tetraphosphate solution has been attributed to complexation between it and phosphate chain anion (WATTERS et al. 1963). In the present paper preparation of some polyphosphates of organoaminium cations have been reported. The composition and polymeric nature

(structure Ia to f and 2) of these derivatives were established by end-group titration, viscosity and conductance measurements.

$$\left[\begin{array}{c} O \\ \| \\ P - O \\ | \\ O^-H_3^+NR \end{array}\right]_n \quad I$$

where Ia, $R=CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH_2$

Ib, $R=CH_3-CH_2^+.CH_3NH_2$

Ic, $R = CH_3(CH_2)_3NH_2.$

Id, $R = NH_2.NH.CO.NH_2$

Ie, $R = CH_3.NH.CO.NH.CH_3$

If, $R = CH_3(CH_2)_4.NH_2.$

$$\left[\begin{array}{c} O \\ \| \\ P - O \\ | \\ O^-H_2^+N = C \begin{array}{c} NH_2 \\ NH_2 \end{array} \end{array}\right]_n$$

II

Experimental

All the reagents used were of analytical grade. Extra pure water was used for preparing solutions. The organic poly(aminiumphosphate)s were prepared by a precipitation technique as follows. Aqueous solutions of lithium polymetaphosphate and organic salts were mixed in 1:1 mole ratio pH of the solutions were adjusted below 4 units by the addition of 0.01M hydrochloric acid. The lowering of pH was considered necessary on the assumption that at this pH the association of lithium ions with the polyphosphate chain should be negligible, as compared to H^+ ions. The addition of aminium salts will result in the association of organic moiety with the phosphate chain anions. Addition of 2-propanol resulted the formation of a viscous mass which settled down on cooling the turbid solution in an ice bath for half an hour. After decanting out the supernatent liquid it was smeared repeatedly in 2-propanol for extracting as much water out of it as possible. Finally, it was dried at room temperature under reduced pressure. These derivatives were obtained as amorphous, hygroscopic white powders.

The composition of these complex derivatives were established by analysing them for nitrogen and phosphorus. The results of analysis were found in accordance to the composition

(BHPO$_3$). The number average molecular weights(Mn) of these derivatives were determined by end-group titration (GUSTAVSON, LARSSON, 1951) with the help of a pH meter (Systronic type) using a glass and a calomel electrode. The solutions of polyphosphoric acid used in these titrations were prepared by passing the aqueous solution of these derivatives through a column of cation exchange resin (Amberlite IR 45). The values or number average molecular weight(Mn) have been recorded in table 1.

<u>TABLE 1</u>

Molecular weights of organic poly(aminium-phosphate)s derivatives.

	M_n	M_w
Ia. Poly(iso.But-2-aminiumphosphate)	3956	8750
Ib. Poly(n-Prop-1-aminiumphosphate)	3796.6	8465
Ic. Poly(n-But-1-aminiumphosphate)	3518	7897.8
Id. Poly(amino uroniumphosphate)	2820	6562.5
Ie. Poly(N,N'-dimethyluronium-phosphate)	2827.5	6392
If. Poly(n-Pent-1-aminiumphosphate)	2744	6165
II. Poly(iminouroniumphosphate)	3080	6903

The viscosities of the solutions were measured by using an Ostwald viscometer at $32\pm0.1^{\circ}$C The concentration in the range of 0.1 gm to 1.0gm per 100 ml were chosen in 0.035N sodium chloride solution. Densities were measured with a pyknometer of 11 ml capacity. Weight average molecular weight(M_w) values of these derivatives have been calculated by using equation:

$$\eta = k \cdot M_w^{\alpha} \qquad (1)$$

Where η is the intrinsic viscosity and k is a constant(STRAUSS et al. 1953). The values of M_w were recorded in table 1. The conductance(FUOSS, 1951) of these derivatives were measured with the help of a Toshniwal conductivity bridge and a Philips conductivity cell(cell factor 1.49).

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Results and Discussion

The specific as well as relative viscosities have been plotted against concentration (Figure 1) Straight line curves were obtained, which on extrapolation intersect at the same point on y-axis(OHASHI et al. 1963). This kind of behaviour is characteristic of linear polymers. A straight line relationship (Fig. 2) between intrinsic viscosity and M_n values further confirms the reliability of viscometric data (VAN WAZER 1950$_a$). The range of M_w values for these derivatives indicates that the chain line length of the polyphosphate precipitated by organic cations probably depends on the basic nature of amines and their solvent competability. The more basic amines are able to get the higher molecular weight phosphate chains precipitated.

Fig.1 Straight line relationship between specific and relative viscosity and concentration.
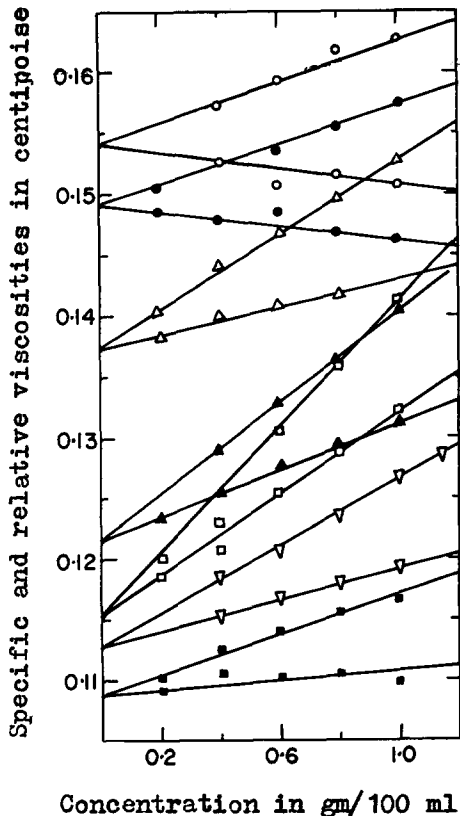
Ia ○, Ib ●, Ic △
Id ◻, Ie ▽, If ▮
II ▲

Specific and relative viscosities in centipoise

Concentration in gm/100 ml

Fig. 2 Straight
line curve bet-
ween intri-
sic viscosity
and M_n

Ia ▲, Ib ▽ ,
Ic ▮, Id ▢ ;
Ie △, If ◇ ;

II ●
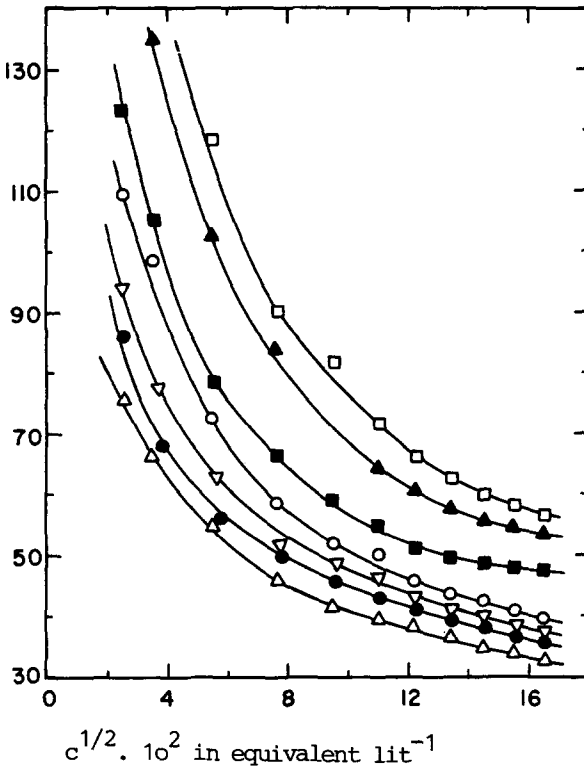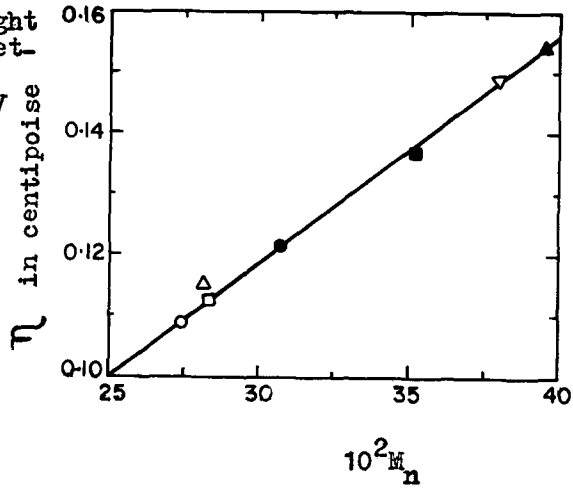
Fig. 3
Plot of
equivalent
conducta-
nce versus
square root
of concen-
tration

Ia △ , Ib ●
Ic ▽ , Id ▲
Ie ▮ , If ▢

II ○

End-group methods have been used to verify the chain length in case of these derivatives. The ratio of M_w/M_n has been used to elucidate the size distribution (VANWAZER 1950b) and found in the range of 2.21 to 2.32. The higher values of above ratio could be ascribed to the lower M_n values. It may be pointed out that the M_n values of these derivatives is much more suscept-ible to hydroly-tic degradation of polyphosphate chain in the presence of aminium cations.

The plot of equivalent conductance versus square root of concentration(Fig. 3) is similar to those of Graham's salt and is typical of polyelec-trolytes(FUOSS 1951).

Acknowledgement

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