Synthesis of some organic poly(aminium phosphate)s: 4.

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Poly(aminium phosphate)s were prepared by precipitation from aqueous solution. The composition of these derivatives was established by analysing for nitrogen and phosphorus. Weight average molecular weights were determined by intrinsic viscosity determination. The intrinsic viscosity has been determined by replacing the usual extrapolation of specific viscosity to zero concentration (η_{sp}/C vs. C–0) with the extrapolation of linear transformation. $G=AF+B$ where $G=y/\alpha-x$, $F=x/\alpha-x$ and $\alpha=x_M+x_m$ (where $y=\eta_{sp}/C$ and x_m and x_M denote concentration). The values for Huggins constants ($k'+k''$) were also calculated and found to be characteristic of linear chain polymers. The R_g values for poly(aminium phosphate)s have been determined in New Ebel's solvent, by a paper chromatographic technique. A linear relationship between degree of polymerization and R_g values is indicative of the linear chain polymeric character of these derivatives. The polyelectrolyte behaviour of these polymers has also been established by conductivity measurements.

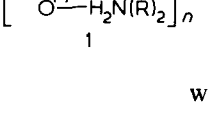
Keywords Synthesis; precipitation; analysis; poly(aminium phosphate); intrinsic viscosity; conductivity

INTRODUCTION

Alkali metal polyphosphate polymers are well known for their suspending, peptizing and detergent[1] actions and behave in a similar manner to organic surfactants. The chemistry of these compounds has been extensively investigated and reviewed by several workers[2–4]. However, the chemistry of poly(aminium phosphate)s has, so far, not been systematically investigated, although their importance as fertilizers[5] and surfactants[1] has been recognized fully.

Recently, ammonium polyphosphates[6] have been prepared by heating ammonium orthophosphate with urea at 170°C in a hydrocarbon solvent. Kobayashi[7] synthesized guanidium condensed phosphates by reaction between dicyandiamide ($H_4C_2N_4$) and ammonium dihydrogenphosphate in an autoclave. A few poly(uronium phosphate)s, of relatively lower molecular weight, have been prepared by Sarbaev *et al.*[5] The preparation of poly(aminium phosphate)s by a precipitation technique[8] have been reported from these laboratories more recently[9,10].

The present paper describes the preparation of some aminium polyphosphate derivatives by a precipitation method from aqueous solutions, their compositions $(BHPO_3)_n$ [where BH^+ = organic cations] and some studies of their polymeric nature.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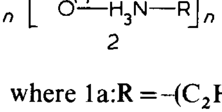
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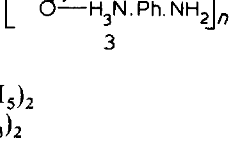
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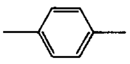
where 1a:R = $-(C_2H_5)_2$
1b:R = $-(CH_3)_2$

and 2a:R = $-(CH_2)_4.(NH_2)CH.COOH$
2b:R = $-\overline{(CH_2)_2.NH.CH_2.CH_2}$
2c:R = $-CO.NH.CONH_2$
2c:R = $-CO.NH.CONH_2$
2d:R = $-(HOOC).CH.CH_2.CONH_2$

3, where Ph = 

EXPERIMENTAL

All the reagents used were of analytical grade (BDH) and were recrystallized before use. Lithium-(polymeraphosphate) used in the reaction was synthesized as described by Mehrotra and Oza[8].

A precipitation technique[8–10] was employed for the preparation of organic poly(aminium phosphate)s. Aqueous solutions of poly(lithium phosphate) and hydrochlorides of amines or amide were mixed in 1:1 mol ratio. The pH of the resulting solution was kept below 4 units by the addition of 0.01N hydrochloric acid solution. It was assumed that below pH 4 the association of lithium ions with the polyphosphate chain should be negligible as compared to the organo aminium cations. The addition of organic amine or amide salts results in an association of organic cations with the polyphosphate chain anions. The addition of 2-propanol to the clear solution led to the formation of a turbid solution from which a viscous mass settled on cooling in an ice bath for about 30 min. After decanting off the supernatant liquid, the viscous mass was smeared repeatedly with 2-propanol for extracting out as much water as possible and to remove lithium salt by solvent extraction. Poly(aminium phosphate)s are obtained as white, amorphous, hygroscopic powders after drying under vacuum at room temperature.

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The number average molecular weights were determined after passing the aqueous solutions of these poly(aminium phosphate)s through a cation-exchange resin (Amberlite-I.R.-45H)[9,10]. The poly(phosphoric acid) produced was titrated with 0.1N sodium hydroxide using a pH meter (systronic type) and a glass and a calomel electrode[11]. The generation of polyphosphoric acid was considered to be essential in view of the observations that the titration of aqueous solutions of individual bases of the same normality, with 0.1N sodium hydroxide in absence of polyphosphate anions, also showed inflections in the pH region 4–5.

The weight average molecular weights (M_w)[12] were determined in 0.035N sodium chloride solution by employing an Ostwald-Viscometer and a pycnometer. The conductivity measurements were carried out by using a conductivity bridge (Toshniwal type) and a Philips conductivity cell (cell factor 1.49). Paper chromatographic[13] analysis was performed in a New Ebel's[14] solvent using Whatman (number one) chromatographic paper.

RESULTS AND DISCUSSION

The viscosity determination of these organo poly(aminium phosphate)s were carried out in 0.35N and 0.07N sodium chloride solutions. A plot of (*Figure 1*) reduced viscosity (η_{sp}/C) and inherent viscosity $(\ln \eta_r/C)$ *versus* concentration on the same graph extrapolates to the same point on the Y axis, indicating that the poly(aminium phosphate)s are linear chain polymers[15]. For linear chain polymers, the viscosity data are expressed as a function of concentration by Huggin's equation,

$$\eta_{sp}/C = [\eta] + k'[\eta]^2.C. \qquad (1)$$

An entirely identical equation is:

$$\ln \eta_r/C = [\eta] - k''[\eta]^2,C, \qquad (2)$$

where k' and k'' are Huggin's constants, having the values

$$k' + k'' = 1/2$$

Table 2 contains the values of constants k' and k'' the sum of which corresponds to 0.5 to 0.6 which is characteristic of linear chain polymers.

Based on Staundinger's law, Strauss[16] derived a relationship between weight average molecular weight of Graham's salt and its intrinsic viscosity in 0.035N sodium bromide solution. It can be expressed according to the equation

$$(\eta_{sp}/C)_{c\to 0} = [\eta] = K.M_w^a \qquad (3)$$

where K and a are constants and M_w is the weight average molecular weight. The value of K determined by light scattering corresponds to 1.76×10^{-5}. Mehrotra and Gupta[17] used 0.035N sodium chloride solution instead of sodium bromide as a supporting electrolyte for determining the molecular weight of the Graham's salt. The use of sodium chloride as the theta solvent was based on the fact that the anionic part of the supporting electrolyte did not appear to play any noticeable part in the suppression of the ionic charge on polyelectrolyte chain as evidenced by the viscometric studies of these workers and those of Chatterjee and Bhargava[18].

The value of K was rechecked by Gupta[17] in 0.035N sodium chloride and was found to be the same within experimental errors as given by Strauss *et al.*[16] Even the cationic part of the supporting electrolyte does not appear to affect the M_w values of the above constant appreciably. This was shown by Strauss and coworkers[12] who have determined the molecular weight of lithium polymetaphosphate by intrinsic viscosity measurements in sodium bromide and lithium bromide solutions. They found that the observed values fall within the range of the molecular weights obtained by light scattering studies. Hence in the viscometric studies of organo-poly(aminium phosphate)s 0.035N sodium chloride has been used as a supporting electrolyte and the value of K equal to 1.76 $\times 10^{-5}$ has been employed while calculating the weight average molecular weights (M_w). The M_w values for various poly(aminium phosphate)s are recorded in *Table 1*.

Nagy *et al.*[19] have suggested an improved graphical method for the determination of M_w values of polymers. It has been suggested that the reliability of the determination of M_w from viscometric data is considerably improved by replacing the extrapolation of the usual equation

$$y = ax + b \qquad (4)$$

(which corresponds to the plot of η_{sp}/C vs. c and parameters a and b are slope and intercept respectively).

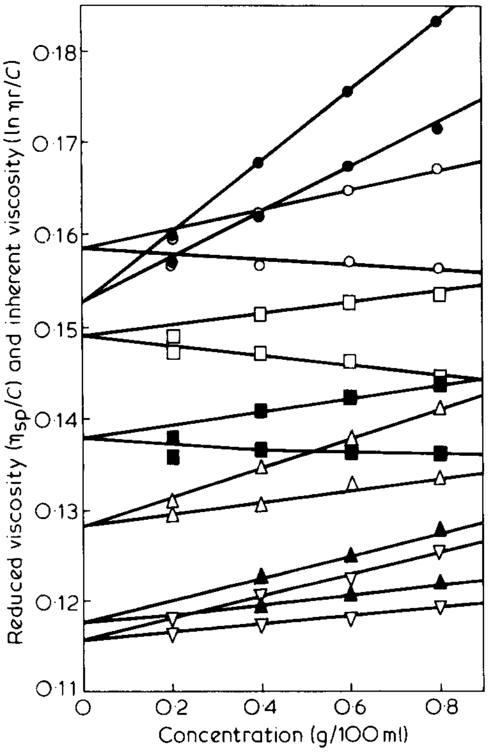

Figure 1 Plot of reduced viscosity (η_{sp}/C) and inherent–viscosity $(\ln \eta_r/C)$ *versus* concentration. (●) 1a, Poly(diethyl aminium phosphate); (○) 1b, Poly(dimethyl aminium phosphate); (■) 2a, Poly(1-carboxy, 1-aminopentyl-5-aminium phosphate); (□) 2b, Poly(diethyl-1-amino(4-aminium phosphate); (△) 2c, Poly(ureido formamidium phosphate); (▲) 2d, Poly(1-amido-2-carboxy ethyl aminium phosphate); (△) 3, Poly(1-amino-anilinium phosphate)

Table 1 Number average molecular weight (M_n), weight average molecular weights (M_w and M_w*) and values for intrinsic viscosities of poly(aminium phosphate)s

Substance		M_n	[η] *	M_w	G **	M_w*
Poly(diethyl aminium phosphate), ($C_4H_{12}NO_3P)_n$, (153)	1a	3951	0.1585	9005	0.160	9090
Poly(dimethyl aminium phosphate), ($C_2HNO_3P)_n$, (125)	1b	3831	0.1530	8693	0.155	8806
Poly(1-carboxy, 1-aminopentryl 5-aminium phosphate), ($C_6H_{15}N_2O_5P)_n$, (226)	2a	3445	0.1377	7826	0.140	7950
Poly(diethyl-1-amino-4-aminium-phosphate) ($C_4H_{11}N_2O_3P)_n$, (166)	2b	3720	0.1490	8465	0.152	8660
Poly(ureido formamidum phosphate) ($C_2H_5N_3O_5P)_n$, (183)	2c	3270	0.1285	7301	0.130	7386
Poly(1-amido-2-carboxy ethyl-aminium phosphate) ($C_4H_9N_2O_6P)_n$, (212)	2d	3048	0.1180	6704	0.120	6818
Poly(1-amino-anilinium phosphate) ($C_6H_9N_2O_3P)_n$, (188)	3	3000	0.1160	6590	0.118	6704

* Obtained from the usual expression η_{sp}/C vs. C

** Obtained from the proposed transformation $G = AF + B$

Table 2 Intrinsic viscosity values in 0.035N and 0.07N sodium chloride solution and average $k' + k''$ values of various poly(aminium phosphate)s

	0.035N	0.07N	average $k' + k''$
1a	0.1585	0.1535	0.50
1b	0.1530	0.1450	0.50
2a	0.1377	–	0.53
2b	0.1490	0.1400	0.54
2c	0.1285	–	0.46
2d	0.1180	0.1107	0.52
3	0.1160	–	0.62

With the extrapolation of the linear transformation,

$$G = AF + B \tag{5}$$

where the variables F and G are defined as

$$F = \frac{x}{\alpha - x} \quad \text{and} \quad G = \frac{y}{\alpha - x} \tag{6}$$

where $y = \eta_{sp}/C$, x is the concentration and α is the sum of x_m and x_M, i.e., minimum and maximum concentrations. By the application of equations (5) and (6), the parameters A (slope) and B can be calculated as

$$a' = A - B \quad \text{and} \quad b' = B\alpha \tag{7}$$

where the parameters A (slope) and B (intercept) are determined from this linear transformation (*Figure 2*) respectively and provides better reliability results than by the application of equation (4) only. The values of b' correspond to improved values of intrinsic viscosity determined with the help of equation (7). It is indicated as $[G_n]$, distinguishing it from the intrinsic viscosity values $[\eta]$ obtained by the extrapolation of η_{sp}/C *versus* concentration curves. The values for $[\eta]$, obtained from η_{sp}/C vs. C plot) and $[G_n]$ (obtained from equation (7)) are recorded in *Table 1*. The values of $[\eta]$ and $[G_n]$ differ by 2–4% only. As the molecular weight of polyphosphate polymers varies in the range 10^2 to 10^4, the $[G_n]$ values for molecular weight determination can be used with more reliability. This is reasonable, in view of the fact that at lower concentration of polymers the graph for η_{sp}/C vs. c deviates from straight line. Hence, the weight average molecular weights of poly(aminium phosphate)s can be determined by using the value of $[G_n]$ instead of $[\eta]$ in the equation:

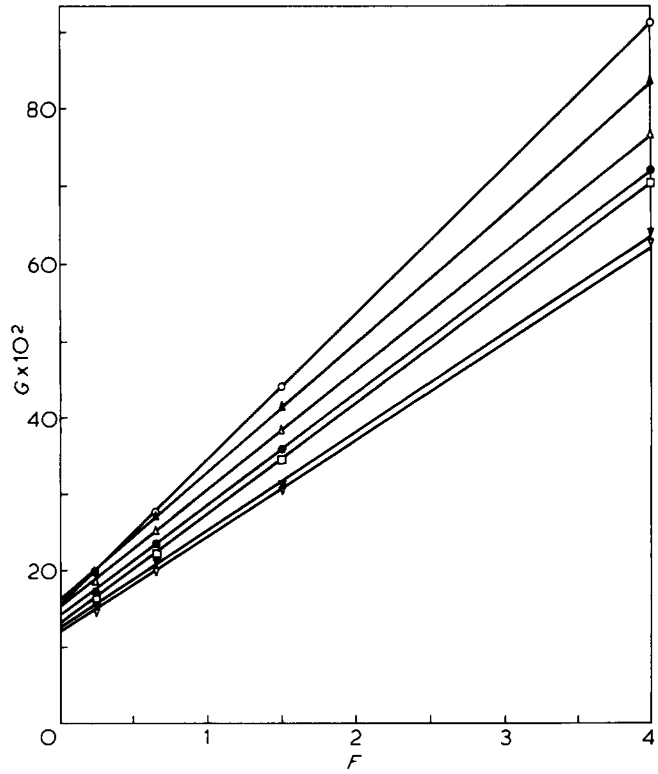

Figure 2 Plot of transformed *G versus F* of the measurements presented in *Figure 1* (α = 1.0 g/dl). 1a, (▲); 1b, (○); 2a, (●); 2b, (△); 2c, (□); 2d, (▲); 3, (△)

$$[G_n]_{c \to 0} = \eta / x_m + x_M$$

$$\text{therefore} \quad (x_m + x_M).[G_n] = 1.76 \times 10^{-5}.M_w^* \tag{8}$$

In this equation $[G_n]_{c \to 0}$ is equal to B (the intercept in *Figure 2*), and $x_m + x_M$ is equal to 1. Hence, the value of α equal to one has been used in these calculations for F and G in equation (6). The M_w values computed according to this procedure are given in *Table 1*.

The viscosity of poly(aminium phosphate) derivatives have also been determined in 0.07N sodium chloride solution[20]. It has been found that values of intrinsic

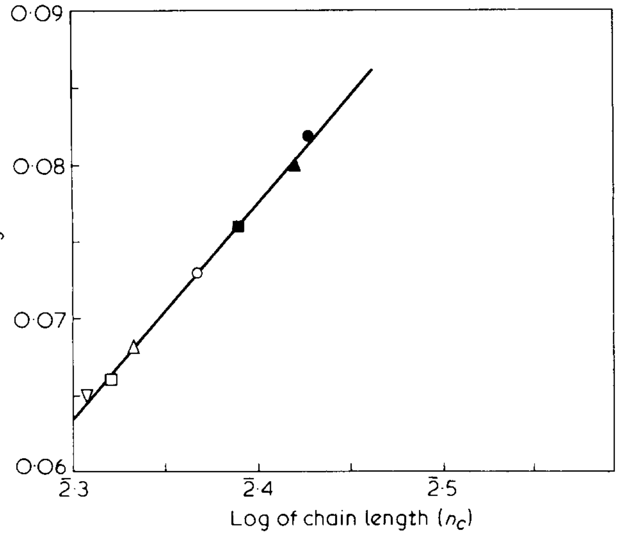

Figure 3 **Straight line plot between R_g values and the negative log of chain length 1a, (□); 1b, (▽); 2a, (○); 2b, (△); 2c, (■); 2d, (▲); 3, (●)**

viscosity [η] decrease in the presence of 0.07N sodium chloride solution. It shows that the increased concentration of supporting electrolyte affects the draining behaviour of these polymers. The values of [η] both in 0.035N and 0.07N sodium chloride solutions are recorded in *Table 2*.

The number average molecular weights (M_n) were determined by the end group titration[8-10] method as described earlier. The M_n values for these poly(aminium phosphate)s are recorded in *Table 1*. The ratio of M_w/M_n corresponds to 2.1 to 2.3. This indicates a most probable distribution for these polymers: Van Wazer *et al.*[21] have shown that molecular weights show a Poisson distribution in case of long chain alkali metal polyphosphates. The conclusion rests on an approach used by Flory[22] in considering the random reorganization in linear organic polymers. It was assumed that terminal phosphate groups of the P–O–P chain are not involved in the reorganization process, since a Poisson distribution for a middle group in the chain is indicated. Ohashi *et al.*[20] determined the viscosities of sodium phosphate and Graham salt. It has been stated that distribution of molecular weights is not exactly the Poisson distribution for lower molecular weight (lower than 1000) samples. In general for a polydisperse polymer:

$$M_w > M_v > M_n$$

with differences increasing as the molecular weight distribution broadens. The ration M_w/M_n can be taken as a measure of distribution of molecular weight in a polymer sample. This ratio is approximately two for polymers having a 'most probable distribution' as expected in case of step reactions (condensation–polymerization)[23]. As poly(aminium phosphate)s have been isolated by reacting poly(lithium phosphate)s having weight average molecular weights in the range 8000–10 000. The ratio of M_w/M_n for these polymers is also more than two. Therefore, it can be predicted that molecular weight distribution for poly(aminium phosphate)s is not exactly Poisson and corresponds to a 'most probable distribution' as expected in case of linear chain polymers.

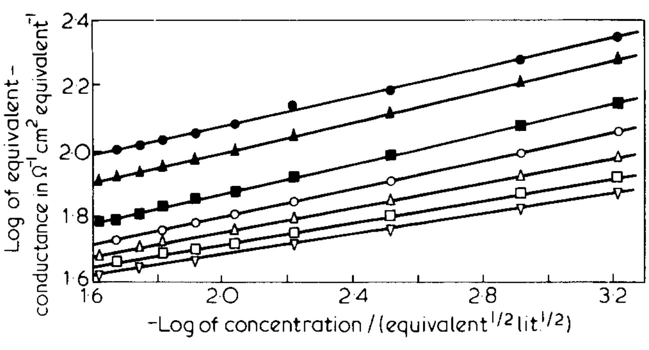

Figure 4 **Plot of log of equivalent conductance *versus* negative log of concentration. 1a, (□); 1b, (▽); 2a, (○); 2b, (△); 2c, (■); 2d, (▲); 3, (●)**

Paper chromatographic analysis of poly(aminium phosphate) derivatives was considered useful for elucidating the purity and hydrolytic stability of the products in aqueous solution. Chromatograms of these derivatives were run in new Ebel's[14] solvent. The chromatograms of all these derivatives show three spots. The R_f and R_g values for the polyphosphate fraction closely correspond to those of poly(lithium phosphate) and Graham's salt. The spots due to *ortho* and tri-*m*-phosphate are produced due to initial hydrolysis of polyphosphate chains in aqueous solution as already reported by several workers. However, the intensity of the spots due to *ortho* and tri-*m*-phosphate is very low in comparison with that of the polyphosphates. A plot of (*Figure 3*) R_g values *versus* the negative logarithm of chain length ($\bar{n}$) gives a straight line relationship. The R_g values varies with chain length of poly(aminium phosphate) derivatives.

A plot of log of equivalent conductance *versus* the negative log of concentration (*Figure 4*) gives straight lines. Such behaviour is characteristic of a polyelectrolyte and can be interpreted on the basis of the Fuoss[24] model, i.e. a chain-like configuration.

All these studies confirm that poly(aminium phosphate)s are polymeric in nature and consist of chains of $(PO_3^-)_n$ repeating units. Different polyphosphates of varying chain length are precipitated depending upon the basicity and solvent compatibility of the aminium cations.

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