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DETERMINATION OF AVERAGE CHAIN LENGTH OF LINEAR POLYPHOSPHATES BY ISOTACHOPHORESIS

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SUMMARY

The relationship between the logarithm of the corrected average chain length, $\bar{n}_c$, of linear polyphosphates and the corrected zone length, C_c, obtained by isotachophoresis was found to be linear; however, an inflection was discernible at $\bar{n}_c$ near 7 and the slope in the range of $n_c > 7$ was higher than that for $\bar{n}_c < 7$. The rapid determination of the average chain lengths of various linear polyphosphates is thereby facilitated without the need to correct for the pressure of ortho- and cyclic phosphates.

INTRODUCTION

The linear polyphosphates are represented by the general formula $M_{n+2}P_nO_{3n+1}$ where M corresponds to a univalent metal[1]. They are usually separated by ion and paper chromatography and then determined by colorimetry[1,2]. However these methods are laborious and time-consuming. Recently, other methods, *e.g.*, high-performance liquid chromatography and an automatic phosphate analyzer[3,4], have been investigated.

We have studied the separation and quantification of the various phosphorus oxoacids by the use of isotachophoresis[5]. The short-chain phosphates (n = 1–3) were separated and determined (*cf.*, Table I). However, the PU values of the long-chain polyphosphates higher than tetraphosphate ($n \geqslant 4$) were so close that their separation was difficult.

In general, the long-chain polyphosphates are present as a mixture with oligophosphates of different chain lengths, and hence the average chain length, $\bar{n}$, is usually employed to characterize them[1,2,6–8].

In this work, a rapid and simple procedure for the determination of the average

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chain length in mixtures of polyphosphates was achieved by means of isotachophoresis.

EXPERIMENTAL

Isotachophoresis

Isotachophorograms were recorded on a Shimadzu IP-2A equipped with a potential gradient detector (PGD). The capillary tubes used consisted of a main column (100 × 0.5 mm I.D.) and a pre-column (100 × 1.0 mm I.D.). The migration current was statilized at 100 μA after 200 μA for 12 min, and the oven temperature was 25°C. The recorder chart speed was 40 mm/min.

The leading and terminating solutions were 0.01 *M* hydrochloric acid–histidine–0.1% Triton X-100, pH 5.5, and 0.01 *M* hexanoic acid, respectively.

Preparation of polyphosphates with different average chain lengths

NaH_2PO_4 and Na_2HPO_4 were mixed to give different Na/P mole ratios, then about 15 g of the mixture were heated for 1 h at 800°C in a platinum dish. The melt was poured onto a stainless-steel cooled in an ice-bath.

End-group titration and determination of average chain length

About 1 g of the chain polyphosphates was dissolved in 100 ml water, and 10 ml of the solution was passed down a column of cation-exchange resin (H^+). The effluent was titrated with a standard solution of sodium hydroxide. The average chain length, $\bar{n}$, was calculated from the values of the titre at up to pH 4.6, *A*, and from 4.6 to 9.6, *B*, as follows[1,6]:

$$\bar{n} = \frac{2(\text{total P})}{(\text{end-group P})} = \frac{2A}{B} \tag{1}$$

Determination of content of P_1 and P_{3m} by isotachophoresis and correction of $\bar{n}$

The sample solutions used in the end-group titration were diluted five times and 5 μl of the resultant solution were applied in isotachophoresis.

Fig. 1. shows an isotachopherogram of polyphosphate. P_1 and P_{3m} can easily be separated from other phosphates because P_1 has the largest PU value and P_{3m} the smallest, and hence their contents can be calculated from the titre *A* and two values, *a* and *b*, obtained from the isotachophorogram

$$P_1(\%) = \frac{7.81 \cdot 10^{-10} \times a}{A_c} \cdot 100 \tag{2}$$

$$P_{3m}(\%) = \frac{3.70 \cdot 10^{-10} \times 3 \times b}{A_c} \cdot 100 \tag{3}$$

where A_c is the number of moles of phosphates in the injected volume (5 μl), *i.e.*, $A_c = (A/1000) \cdot (\text{concentration of standard sodium hydroxide solution}) \cdot (1/5) \cdot$

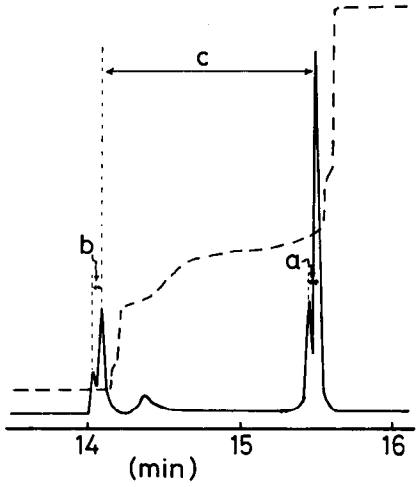

Fig. 1. Isotachopherogram of polyphosphate including P_1 and P_{3m}.

$(5 \cdot 10^{-3}/10)$; and $7.81 \cdot 10^{-10}$ and $3.70 \cdot 10^{-10}$ are numbers of moles per unit zone length (mm) in the isotachophorogram for P_1 and P_{3m}, respectively.

The corrected average chain length, $\bar{n}_c$, in which a weak acidic H of P_1 was corrected and P_{3m} was removed, is given by:

$$\bar{n}_c = \frac{2A(1 - P_{3m}\%/100)}{B + A \cdot P_1\%/100} \tag{4}$$

Preliminary polyphosphates hydrolysis experiments

It is well known that polyphosphates hydrolyse in aqueous solution[1,2,7] Lúčanský and Bátora[9] reported the hydrolysis of polyphosphates during isotachophoretic analysis. We examined the effect of hydrolysis in the leading solution on the average chain length and the zone length, and confirmed that there was no influence of hydrolysis within 24 h of dissolution of the polyphosphate samples.

RESULTS AND DISCUSSION

For short-chain phosphates with $n = 1$–4, the zone length per mole of P decreased with increasing number of P atoms, *i.e.*, n, as shown in Table I. It might therefore have been expected that the zone length per mole of P would decrease with increasing chain length. The PU values of polyphosphates higher than tetraphosphate were found to lie between the values of P_{3m} and P_1 (*cf.*, Table I).

Fig. 2 shows the relationship between the logarithm of the corrected average chain length, $\log \bar{n}_c$, and the corrected zone length, C_c:

$$C_c = C/(A_c - A_c \cdot P_{3m}\%/100)$$

TABLE I

PU VALUES AND ZONE LENGTHS OF SHORT-CHAIN PHOSPHATES

Phosphate	*PU value*	*Zone length (mm per mole of P)*
P_1	0.669	1.28×10^9
P_2	0.306	1.06×10^9
P_3	0.227	0.93×10^9
P_4	0.233	0.80×10^9

It is seen that $\log \bar{n}_c$ decreases linearly with C_c, but the slope changes abruptly at $\log \bar{n}_c = 7$. The two straight lines can be expressed as:

$$\log \bar{n}_c = -0.258C_c + 2.310; \bar{n}_c = 1\text{–}7 \quad (5)$$

$$\log \bar{n}_c = -0.114C_c + 1.494; \bar{n}_c \geqslant 7 \quad (6)$$

Van Wazer[1,8] showed that long-chain phosphate anions exhibit a coiled structure. Our results suggest that the shorter chain phosphate anions may be rigid because of their high charges and the longer ones flexible because of their longer chains. The geometric form of polyphosphate anions in solution is considered to depend on the nature and concentration of the electrolyte, and on the pH of the leading solution. In the present leading solution, $\bar{n}_c$ about 7 seems to be a critical chain length on the boundary between rigid and flexible forms.

On the other hand, the average chain lengths of polyphosphates have been determined by end-group titration, viscosity and light-scattering studies and thermoanalysis[6–8,10–15]. The end-group titration method was mainly employed for polyphosphates such as Graham's salt. When orthophosphate and cyclic phosphates are

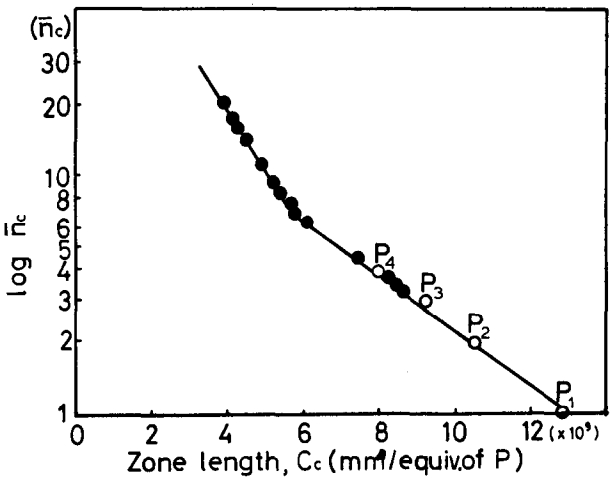

Fig. 2. Relationship between zone length and average chain length. P_1, P_2, P_3 and P_4 are pure samples of ortho-, pyro-, tri- and tetraphosphate, respectively.

included in a sample, the average chain length obtained must be corrected to take account of their presence. Although the average chain length, $\bar{n}$, of polyphosphates can be calculated by eqn. 1, Van Wazer[1] proposed that if P_1 and cyclic phosphates are present the value of $\bar{n}$ must be corrected according to:

$$\bar{n} = \frac{2(\text{total P} - P_1 - \text{cyclic P})}{(\text{end-group P} - P_1)} \tag{7}$$

For a series of linear polyphosphates it is preferable that cyclic phosphates are first removed and P_1 is regarded as a member of the polyphosphates[16].

Unless P_1 and cyclic P are present in a sample, the end-group titration is an effective and simple method for the determination of average chain length in polyphosphates. However, polyphosphates, *e.g.*, Graham's salt, frequently contain a small amount of cyclic phosphates, mainly P_{3m}. Their content must be measured by paper chromatography, etc. and the value of $\bar{n}$ then corrected as in eqn. 7.

On the other hand, since the zone length, C, in isotachophoresis is independent of the end-group of the phosphates and does not include the zone length of P_{3m}, we can be rid of the above troublesome correction and easily determine $\bar{n}_c$ from eqn. 5 or 6, or Fig. 2. The $\bar{n}_c$ value obtained can be regarded as the average chain length for all polyphosphate anions, including P_1 but with cyclic phosphate (P_{3m}) removed, while the value of $\bar{n}$ in eqn. 7 does not include P_1.

Thus, the average chain length of polyphosphates was determined rapidly by isotachophoresis without analyses for P_1 and P_{3m}, and correction by means of eqn. 7. The content of P_{3m} could also easily be found because the PU value of P_{3m} was the smallest of all the phosphate anions as shown in Fig. 1.

Application

The $\bar{n}_c$ values of some commercial polyphosphates were deteremined by the

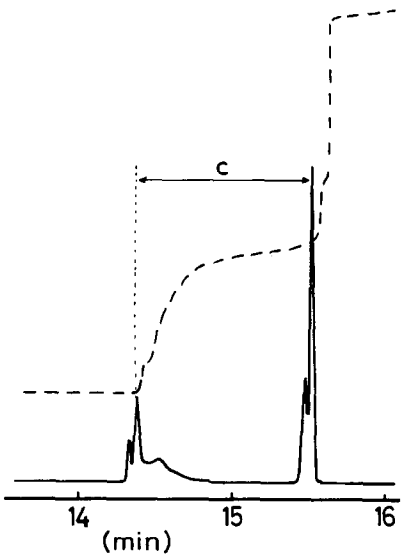

Fig. 3. Isotachopherogram of commercial polyphosphate.

TABLE II

COMPARISON OF RESULTS FOR SOME COMMERCIAL SAMPLES

ITP = Isotachophoresis; ET = end-group titration.

Sample	*ITP*	*ET*		P_1(%)	P_{3m}(%)
	$\bar{n}_c$	$\bar{n}$	$\bar{n}(P_1,P_{3m})$*		
1	3.0	4.1	3.1	14.8	2.4
2	6.9	9.1	7.3	4.2	4.2
3	12.3	13.4	12.8	**	4.3
4	10.5	11.0	9.9	1.4	3.7
5	11.2	11.9	11.5	**	3.9
6	6.4	8.7	5.9	9.3	3.8
7	13.0	14.6	12.6	1.4	5.0

* Average chain length corrected for P_1 and P_{3m} using eqn. 4.
** Below the limit of detection (0.3%).

present procedure. About 0.2 g of the sample were dissolved in 100 ml of water and 5 μl of the solution were placed in the isotachoanalyzer.

Fig. 3 shows a typical isotachophorogram of the commercial sample. The value of $\bar{n}_c$ was determined from the zone length, C_c, using eqn. 5 or 6, or Fig. 2.

Unless the total amount of P atoms in the sample was known, it was measured as follows. The above sample solution (100 ml) was boiled for 30 min with 6 *M* hydrochloric acid (2 ml) to hydrolyse completely all of the condensed phosphates. The hydrolysed solution was then diluted to 100 ml and analysed for the total amount of P atoms by isotachophoresis.

The values of $\bar{n}_c$ obtained by isotachophoresis and those of $\bar{n}$ by the end-group titration method are given in Table II. It is seen that the two sets of values were in good agreement except for three samples (1, 2 and 6) which contained relatively large amounts of P_1 and P_{3m}. If P_1 and P_{3m} were taken into account, their average chain length, $\bar{n}(P_1, P_{3m})$, was in accordance with $\bar{n}_c$ obtained by IP.

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