Intrinsic Viscosity–Molecular Weight Relationships in Copolyphosphates

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ABSTRACT: A number of samples of sodium potassium (Na : K = 9 : 1 to 3 : 7) and lithium potassium (Li : K = 9 : 1 to 5 : 5) copolyphosphates were prepared and characterized. Their number-average molecular weights were determined by end-group titration and intrinsic viscosities were determined in 0.035 N NaBr solution. Intrinsic viscosity–molecular weight relationships according to the Mark–Houwink equation were established for each series of compounds. A highly interesting feature of the results obtained was a decrease in the value of the constant a with an increase in the mole fraction of potassium in the copolyphosphates. This is a remarkable demonstration of the dependence of a on the degree of solvation; the solubilities of both kinds of copolyphosphates were found to decrease with an increase in the proportion of potassium.

KEY WORDS   Sodium Potassium Copolyphosphates / Lithium Potassium Copolyphosphates / Intrinsic Viscosity / Molecular Weight / Mark–Houwink Equation /

The long chain polyphosphates have been prepared and characterized by a number of workers over the last several decades.[1–3] The techniques generally employed for determining their molecular weights include light scattering,[4,5] end-group titration,[6,7] and viscosity.[4,7] Bhargava et al.[5,7,8] have used all these techniques in a number of cases involving simple polyphosphates and Mehrotra et al.[9] used the technique of end-group titration and viscosity in the case of compounds which could be termed 'copolyphosphates.' These are counter cation copolymers containing two kinds of cations attached to a polyphosphate chain -P-O-P-O-P-O, etc. Mehrotra et al.,[9] however, simply used the intrinsic viscosity [η]–weight-average molecular weight (M_w) relationship given by Strauss et al.[4] for sodium

polyphosphates without realizing that it could not hold good in the case of other poly- and copolyphosphates. In the present work [η]-M_n relationships were obtained for a number of copolyphosphates having two cations. One series of compounds had sodium and potassium in molar ratios varying from 9 : 1 to 3 : 7 and another series had lithium and potassium in molar ratios 9 : 1 to 5 : 5. While NaPO$_3$ and KPO$_3$ units made up the former copolyphosphates, LiPO$_3$ and KPO$_3$ units were interlinked in the latter ones.
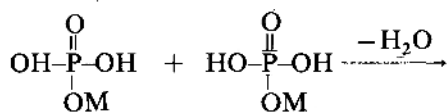
EXPERIMENTAL

Materials and Methods

(i) *Preparation of Sodium-Potassium Copolyphosphates (NaKPP).*[*1]   Both NaH$_2$PO$_4$

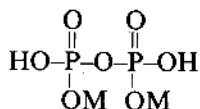* To whom correspondence should be sent.
** Present address: *Chemistry Department, Jahanabad College, Jahanabad, Bihar, India.*
*1 The abbreviation Na*K*PP is used throughout this paper to describe compounds having sodium and potassium cations attached to the polyphosphate chain.

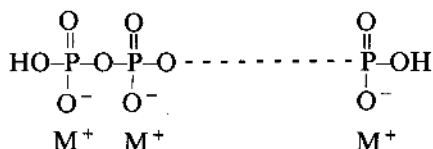and KH_2PO_4 polymerize on heating at temperatures higher than 400°C.

$$OH\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\displaystyle OM}{|}}{P}}OH \ + \ HO\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\displaystyle OM}{|}}{P}}OH \ \xrightarrow{\ -H_2O\ }$$

Orthophosphate Orthophosphate

$$HO\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\displaystyle OM}{|}}{P}}O\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\displaystyle OM}{|}}{P}}OH$$

Pyro- or Diphosphate

The condensation polymerization reaction ultimately leads to the formation of a high polymer.

$$HO\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\underset{\displaystyle M^+}{\displaystyle O^-}}{|}}{P}}O\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\underset{\displaystyle M^+}{\displaystyle O^-}}{|}}{P}}O\text{--------}\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\underset{\displaystyle M^+}{\displaystyle O^-}}{|}}{P}}OH$$

This can be written as $H(MPO_3)_nOH$ or simply as $(MPO_3)_n$. M^+ represents monovalent cation.
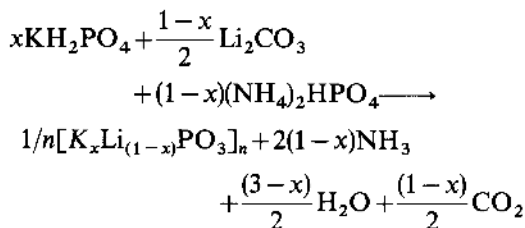
In all the cases the chemicals used were of analytical grade obtained from reputed firms.

A reaction mixture of sodium dihydrogen orthophosphate and potassium dihydrogen orthophosphate required, taken in different molar ratios ranging from 9:1 to 3:7, was mixed thoroughly and placed in a platinum dish. The whole thing was heated in a Gallenkamp Muffle Furnace for a desired duration of time at a fixed temperature in the range of 700—850°C. A clear molten liquid was obtained after heating the mixture, which was quickly quenched by pouring on cool surface of a stainless steel plate and quickly pressing another on it. Clear glassy products were obtained. They were powdered, dried in an oven at 100°C, placed in a sample tube, and stored in a desiccator. All the glassy products were transparent and colourless and were easily soluble in water.

(ii) *Preparation of Lithium-Potassium Co-polyphosphates (LiKPP).*[2] For preparing LiKPP samples a reaction mixture of lithium carbonate, potassium dihydrogen orthophosphate and diammonium hydrogen phosphate, required in different Li:K molar ratios, ranging from 9:1 to 5:5 was taken in a platinum dish and mixed well with the help of a glass stirrer. A set of five to six samples with similar Li:K ratios were prepared. In every case the mixture was first heated gradually in an oven at a temperature of 150—200°C, taking care that the material does not spurt out in the initial stages when frothing takes place due to brisk evolution of ammonia, carbon dioxide and water vapour. After the frothing subsided the crucible was placed in a Gallenkamp Muffle Furnace, already heated to the desired temperature in the range 700—900°C for desired durations of time. The muffle furnace was capable of maintaining temperature within ± 10°C.

The chemical reaction leading to the formation of lithium potassium copolyphosphate can be represented as follows:

$$xKH_2PO_4 + \frac{1-x}{2}Li_2CO_3$$
$$+ (1-x)(NH_4)_2HPO_4 \longrightarrow$$
$$1/n[K_xLi_{(1-x)}PO_3]_n + 2(1-x)NH_3$$
$$+ \frac{(3-x)}{2}H_2O + \frac{(1-x)}{2}CO_2$$

The products were all obtained in the form of clear molten liquids which, after heating for various durations of time, were chilled between two stainless steel plates in contact with ice-cooled water. The temperature of preparation and the time during which the mixture was kept in the muffle furnace are given in Table II. In all the cases the glassy product obtained on quenching was dried in an oven at 100°C, powdered, placed in a sample tube and

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[2] The abbreviation LiKPP will be used throughout this paper to describe compounds having lithium and potassium cations attached to the polyphosphate chain.
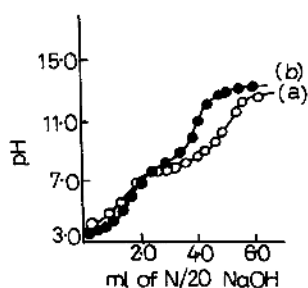
Figure 1. Typical titration curves for samples of co-polyphosphates. (a) sample No. 1, Table I; (b) sample No. 26, Table I.

stored in a desiccator.

(iii) *Determination of End-Group Molecular Weights.* The pH was measured in all titrations by a glass electrode and a calomel half cell, a model 335 digital Systronics pH-meter with an accuracy of ± 0.01 being employed. Carbonate free $0.1\,N$ NaOH solution was used as a base. Titrations were carried out as quickly as possible to avoid contamination with atmospheric carbon dioxide. The solution was also stirred continuously with the help of a magnetic stirrer while adding alkali from a microburette.

In the case of NaKPP samples, a 1% solution was prepared in conductivity water. Since the pH of the freshly prepared solutions ranged from 6.0 to 7.0, this solution was acidified to bring the pH to between 3.0 to 4.0. In each case 25 ml of a 1% solution of the copolyphosphate in question was titrated against the base up to a pH of about 11.0. Two typical plots are given in Figure 1.

The determination of end-group molecular weight was based on the fact that there is one weak acid hydroxyl group at each end of the polymer chain, all other hydroxyl groups are strongly acidic.[1]

The weak acid groups titrate in the pH interval, between two points of inflexion (at pH 5 and 9). The number average molecular weight M_n is given by [6,7]

$$M_n = \frac{20000w}{a} \qquad (1)$$

where w is the weight of the copolyphosphate sample in gram and a is the volume of $0.1\,N$ NaOH in cm^3 needed for titration between the two points of inflexion in a curve obtained by plotting pH against the volume of alkali added.

In the case of LiKPP samples the end-group molecular weight was determined by a method similar to that described by Greenfield and Clift.[10] A freshly prepared 2% solution of the copolyphosphate in conductivity water was taken. A 25 ml aliquot was diluted to 100 ml and the pH adjusted to about 3.0 by adding drop by drop $1\,N$ hydrochloric acid. It was then titrated between pH 4.5 and 9.5 with $0.1\,N$ sodium hydroxide solution (V_1).

A 10 ml aliquot was hydrolyzed by boiling on a sand bath with 25 ml of $3\,N$ nitric acid for at least 30 min. It was then partially neutralized to pH 2—3 with approximately $3\,N$ sodium hydroxide solution and finally titrated between pH 4.5 and 9.5 with $0.1\,N$ sodium hydroxide solution (V_2).

The number-average chain length $\bar{n}$ was calculated by using the formula

$$\bar{n} = \frac{5V_2}{V_1} \qquad (2)$$

By multiplying this number-average chain length with formula weight of the LiKPP samples, the number-average molecular weight was obtained.

(iv) *Determination of Intrinsic Viscosity.* The samples of copolyphosphates were dissolved in $0.035\,N$ NaBr and kept for 24 h for attaining stability.[1,2] Their viscosities were then measured by using a Tuan–Fuoss viscometer[11] with a flow time of about 120 s. The intrinsic viscosities were determined in the usual way by plotting reduced viscosity (η_{sp}/c) against concentration (c) and extrapolating the former to zero concentration. A typical plot is shown in Figure 2 for a LiKPP sample. Similar plots were obtained in all other cases.

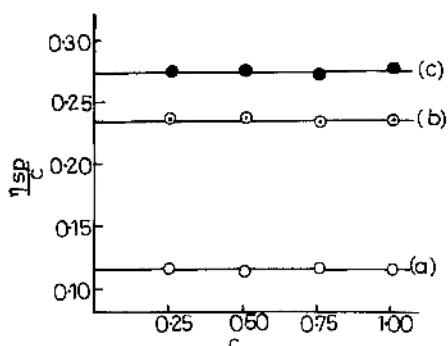When intrinsic viscosities are used for

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Figure 2. Reduced viscosity–concentration curves for samples of LiKPP in $0.035N$ NaBr. (a) sample No. 1; $M_n = 4180$ (Table II) (○); (b) sample No. 10; $M_n = 6360$ (Table II) (◎); (c) sample No. 18; $M_n = 9550$ (Table II) (●).

Table I. Relevant data for samples of sodium potassium copolyphosphates. Duration of heating before quenching was 3 h in each case

| Sample No. | Molar ratio Na : K | Temperature of preparation | M_n | $[\eta]$ |
		°C ± 10°C		
1	2	3	4	5
1	9 : 1	700	4450	0.091
2	9 : 1	750	4555	0.095
3	9 : 1	800	5460	0.108
4	9 : 1	850	6340	0.119
5	8 : 2	700	4500	0.095
6	8 : 2	750	5000	0.105
7	8 : 2	800	7000	0.112
8	8 : 2	850	7500	0.141
9	7 : 3	700	4200	0.085
10	7 : 3	750	6500	0.129
11	7 : 3	800	7500	0.140
12	7 : 3	850	8000	0.150
13	6 : 4	700	4620	0.089
14	6 : 4	750	6000	0.105
15	6 : 4	800	8570	0.131
16	6 : 4	850	8650	0.132
17	5 : 5	700	4800	0.091
18	5 : 5	750	6000	0.105
19	5 : 5	800	8000	0.126
20	5 : 5	850	7055	0.116
21	4 : 6	700	4200	0.085
22	4 : 6	750	7500	0.125
23	4 : 6	800	8000	0.130
24	4 : 6	850	7055	0.117
25	3 : 7	700	4620	0.091
26	3 : 7	750	5000	0.102

determining molecular weights one gets the weight-average or the number-average depending on the kind of average used for calibration as far as the heterogeneities of working and reference samples are approximately the same. According to the well-known Mark–Houwink relationship:

$$[\eta] = KM^a \tag{3}$$

where $[\eta]$ is the intrinsic viscosity, M is the molecular weight, and K and a are constants characteristic of the polymer.

Since a large number of samples of known end-group (number-average) molecular weights were available, the values of K and a could be easily obtained by plotting $\log[\eta]$ against $\log M$.

RESULTS AND DISCUSSION

Molecular Weights and Intrinsic Viscosity-Molecular Weight Relationships

Data giving the conditions of preparation of the copolyphosphates, their number-average molecular weights, and intrinsic viscosities in $0.035N$ NaBr solution are given in Tables I and II. The values of molecular weight were found to lie in the range 4000—9000 in the case of NaKPP samples, while in the case of LiKPP the molecular weights ranged from 4000—10000. In both the cases, an increase in the temperature of preparation usually led to an increase in molecular weight.

The $\log[\eta]$–$\log M_n$ plots were drawn and on the basis of these plots the relationships between intrinsic viscosities and molecular weights as given in Tables III and IV could be calculated.

Table II. Relevant data for samples of lithium potassium copolyphosphate

Sample No.	Molar ratio Li:K	Temperature of preparation °C ± 10°C	Duration of heating before quenching h	M_n	$[\eta]$
1	2	3	4	5	6
1	9:1	700	3	4180	0.115
2	9:1	700	6	6330	0.200
3	9:1	800	3	6630	0.200
4	9:1	800	6	6710	0.250
5	9:1	900	3	6790	0.260
6	9:1	900	6	9000	0.265
7	8:2	700	3	4450	0.155
8	8:2	700	6	4800	0.155
9	8:2	800	3	6220	0.175
10	8:2	800	6	6360	0.235
11	8:2	900	3	6580	0.245
12	8:2	900	6	8370	0.260
13	7:3	700	3	4650	0.125
14	7:3	700	6	5270	0.160
15	7:3	800	3	6220	0.205
16	7:3	800	6	9150	0.230
17	7:3	900	3	9160	0.250
18	7:3	900	6	9550	0.275
19	6:4	700	3	4650	0.150
20	6:4	700	6	4890	0.155
21	6:4	800	3	4960	0.170
22	6:4	800	6	8090	0.215
23	6:4	900	3	8630	0.260
24	5:5	700	3	5190	0.130
25	5:5	700	6	5560	0.145
26	5:5	800	3	6350	0.155
27	5:5	800	6	7590	0.190
28	5:5	900	3	7790	0.190
29	5:5	900	6	9550	0.200

Table III. Intrinsic viscosity–molecular weight relationships for sodium–potassium copolyphosphates

Sample No.	Molar ratio Na:K	Relationship
1	9:1	$[\eta] = 3.6 \times 10^{-5} M_n^{0.93}$
2	8:2	$[\eta] = 1.1 \times 10^{-4} M_n^{0.81}$
3	7:3	$[\eta] = 1.2 \times 10^{-4} M_n^{0.80}$
4	6:4	$[\eta] = 5.7 \times 10^{-4} M_n^{0.60}$
5	5:5	$[\eta] = 7.3 \times 10^{-4} M_n^{0.57}$
6	4:6	$[\eta] = 1.5 \times 10^{-3} M_n^{0.50}$

Table IV. Intrinsic viscosity–molecular weight relationships for lithium–potassium copolyphosphates

Sample No.	Molar ratio Li:K	Relationship
1	9:1	$[\eta] = 7.3 \times 10^{-7} M_n^{1.17}$
2	8:2	$[\eta] = 6.3 \times 10^{-6} M_n^{0.93}$
3	7:3	$[\eta] = 7.3 \times 10^{-5} M_n^{0.89}$
4	6:4	$[\eta] = 2.7 \times 10^{-4} M_n^{0.75}$
5	5:5	$[\eta] = 2.5 \times 10^{-4} M_n^{0.74}$

In NaKPP samples dissolved in 0.035 N NaBr the value of 'a' lies between 0.50 to 0.93. In all LiKPP samples the values of 'a' in salt solution media have been found to lie between 0.74 to 1.17. The value of 'a' = 1.17 is higher than that obtained for sodium polyphosphates ($a = 1$).

The value of a is known to indicate how good or bad the solvent is for a particular polymer–solvent system at a particular temperature.[12] In a theta-solvent in which the solubility is supposed to be minimum and there is little interaction between the solute and the solvent the value of a approaches 0.5. In all other cases its value lies above 0.5 but, particularly in the case of neutral polymers, the maximum value approaches a limit of 0.8.[12,13] However, in the case of polyelectrolytes this limit is quite often exceeded.[14] In the case of NaKPP samples the solubility has been found to decrease with increase in the proportion of potassium and the concentration of salt solution used as θ-solvent is also found to decrease.[15] Similarly, in the case of LiKPP samples also the solubility decreases with increase in the proportion of potassium and the concentration of salt solution used as θ solvent also decreases with decrease in solubility.[16]

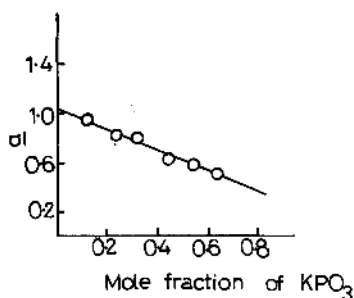The dependence of 'a' on degree of solvation is beautifully illustrated in the plots of mole

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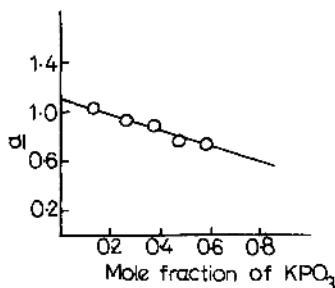**Figure 3.** Plot of a against mole fraction of KPO_3 for NaKPP samples.

Figure 4. Plot of a against mole fraction of KPO_3 for samples of LiKPP.

fraction of KPO_3 against the value of 'a' obtained for both NaKPP as well as LiKPP samples (Figures 3 and 4). In both the cases there is a progressive decrease in the value of 'a' as the mole fraction of potassium increases. As mentioned earlier the solubility of these samples decreased progressively as the proportion of potassium in the copolymer increased. It is perhaps for the first time that such a result has actually been obtained for copolymers.

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