Viscosities of Copolyphosphates in Salt-Free Aqueous Solutions and Theta Solvents I.

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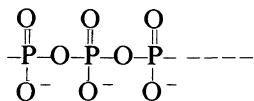*Department of Chemistry, Gorakhpur University, Gorakhpur 273009, India*

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ABSTRACT: The results of viscosity measurements on several samples of lithium–potassium copolyphosphates (Li : K ratio ranging from 9 : 1 to 5 : 5) in salt-free aqueous solutions and in theta solvents are reported. Molecular weights determined by end-group titration ranged from 4000—10000. In aqueous solutions the Fuoss equation parameter A was found to be nearly proportional to the square of molecular weights, indicating rod-like structures of the poly-ions at infinite dilution. The concentrations of NaBr solutions acting as theta solvents at 35°C were determined for all cases and the viscosity data in θ-solvents were utilized in calculating unperturbed dimensions which were found to lie in the range 4.7×10^{-7} cm to 7.4×10^{-7} cm.

KEY WORDS Lithium Potassium Copolyphosphates / Intrinsic Viscosity / Molecular Weight / Theta Solvent / Unperturbed Dimensions /

Viscosity has played a major role in crystallizing our present views on polyelectrolyte shape dynamics. A review by Eisenberg and King[1] also emphasizes its importance in the study of ion-containing polymers. While a number of papers dealing with various aspects of the viscosity behaviour of solutions of long-chain polyphosphates has appeared, none of them presents a detailed study on copolyphosphates, the counter-cation copolymers in which more than one kind of cations are attached to the polyphosphate backbone:

$$\begin{array}{ccc} \overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{-P}}} & \overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{-P}}} & \overset{\displaystyle O}{\underset{\displaystyle |}{\overset{\displaystyle \|}{-P}}} \\ O^- & O^- & O^- \end{array} - - - -$$

Very interesting results have recently been reported by Bhargava *et al*[2] on the intrinsic viscosity molecular weight relationships obtained for sodium potassium and lithium potassium copolyphosphates. As pointed out by Eisenberg and King,[1] viscosity measurements in θ-solvents have been reported only for a few polyelectrolytes. Allen and Watts[3] have pointed out that in amorphous polymers, chains display dimensions which are experimentally indistinguishable from the values obtained in θ solvents, *i.e.*, unperturbed dimensions. The present study reporting viscosity behaviour of lithium potassium copolyphosphates in salt free solutions and θ solvents is, therefore, quite important.
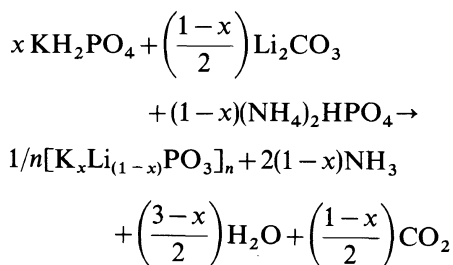
EXPERIMENTAL

Materials and Methods

(*i*) *Preparation of Lithium–Potassium Copolyphosphates (LiKPP).*[*1] To prepare the 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 a glass stirrer. A set

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*1 The abbreviation LiKPP, will be used throughout this paper to describe compounds having lithium and potassium cations attached to the polyphosphate chain.

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 did not spurt out in the initial stages when frothing took 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 a temperature within $\pm 10°C$.

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

$$x\,KH_2PO_4 + \left(\frac{1-x}{2}\right)Li_2CO_3$$

$$+ (1-x)(NH_4)_2HPO_4 \rightarrow$$

$$1/n[K_xLi_{(1-x)}PO_3]_n + 2(1-x)NH_3$$

$$+ \left(\frac{3-x}{2}\right)H_2O + \left(\frac{1-x}{2}\right)CO_2$$

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-cold water. The temperature of the preparation and time during which the mixture was kept in the muffle furnace are given in Table I. In all cases, the glassy product obtained on quenching was dried in an oven at 100°C, powdered, placed in a sample tube and stored in a desiccator.

(ii) *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). A carbonate free 0.1 N NaOH solution was used as a base. Titrations were carried out as quickly as possible to avoid contamination by atmospheric carbon dioxide. The solution was also stirred con-

tinuously with a magnetic stirrer while adding alkali from a microburette.

The end-group molecular weights were determined by a method similar to that described by Greenfield and Clift.[4] 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 using the formula

$$\bar{n} = \frac{5V_2}{V_1} \tag{1}$$

By multiplying this number average chain length by the formula weight of the LiKPP sample in question, the number-average molecular weight was obtained.

(iii) *Determination of Viscosity.* The viscosity was measured with the help of a Tuan-Fuoss viscometer[5] at a flow time of about 120 s. All measurements were done at $35 \pm 0.05°C$ in a thermostat. Before taking any measurements, the solutions of lithium–potassium copolyphosphates were kept for 24 h so as to attain stability.[2,6,7]

(iv) *Determination of Theta (θ) Solvents.* In a theta solvent, there is no interaction between the solute and solvent and the value of the exponent a of the Mark–Houwink equation is equal to 0.5. For polyelectrolytes, a salt solution at a particular concentration is a theta solvent for a particular temperature. In our experiments the temperature was kept at 35°C. Intrinsic viscosities of samples belonging to each series were determined in sodium bromide solutions in the concentration range from

Table I. Fuoss equation parameters

Sample No.	Molar ratio Li:K	Temperature of preparation °C ± 10°C	Duration of heating before quenching/h	$\bar{M}_n$	A	B/A	B	$[\log(A/B+1)]$
1	9:1	700	3	4180	0.7438	6.0460	4.4970	0.2185
2	9:1	700	6	6330	2.1547	3.2310	6.9619	0.4906
3	9:1	800	3	6630	2.2144	3.0143	6.6759	0.5208
4	9:1	800	6	6710	2.2391	2.9594	6.6265	0.5288
5	9:1	900	3	6790	2.4462	2.9070	7.1110	0.5365
6	9:1	900	6	9000	2.3182	1.6299	5.4082	0.7880
7	8:2	700	3	4450	1.7256	4.7037	8.1167	0.3275
8	8:2	700	6	4800	1.8636	4.2319	7.8866	0.3734
9	8:2	800	3	6220	3.2704	2.9438	9.6273	0.5311
10	8:2	800	6	6360	3.3784	2.3539	9.6416	0.5446
11	8:2	900	3	6580	3.5002	2.7211	9.5244	0.5652
12	8:2	900	6	8370	5.7650	1.9433	11.2029	0.7115
13	7:3	700	3	4650	1.2106	4.3976	5.3237	0.3568
14	7:3	700	6	5270	1.4962	3.7010	5.5374	0.4317
15	7:3	800	3	6220	2.3283	2.9438	6.8540	0.5311
16	7:3	800	6	9150	3.6751	1.7283	6.3517	0.7624
17	7:3	900	3	9160	4.7281	1.7253	8.1575	0.7631
18	7:3	900	6	9550	5.4585	1.6292	8.8930	0.7880
19	6:4	700	3	4650	1.7123	4.5872	7.8546	0.3385
20	6:4	700	6	4890	1.8519	4.2808	7.9277	0.3684
21	6:4	800	3	4960	1.9072	4.1981	8.0067	0.3769
22	6:4	800	6	8090	4.7852	2.1478	10.2775	0.6680
23	6:4	900	3	8630	5.4025	1.9798	10.6959	0.7003
24	5:5	700	3	5190	1.6669	4.0783	6.7981	0.3895
25	5:5	700	6	5560	1.7241	3.7189	6.4117	0.4296
26	5:5	800	3	6350	2.0012	3.1124	6.2285	0.5069
27	5:5	800	6	7590	3.1212	2.4510	7.6519	0.6106
28	5:5	900	3	7790	4.3630	4.3669	10.3266	0.6258
29	5:5	900	6	9550	5.0302	1.8015	9.0618	0.7444

0.05 M to 0.50 M. After obtaining the value of a in each case, plots of a vs. concentrations of NaBr were drawn and the concentration of NaBr at which $a = 0.5$ was noted. This gave a θ solvent for 35°C.

## RESULTS AND DISCUSSION

(a) Viscosities in Aqueous Solutions

The values of reduced viscosity (η_{sp}/c) were obtained in conductivity water for all the samples of LiKPP having number-average molecular weights ranging from 4000—10000. Typical η_{sp}/c vs. c curves for some of the samples of LiKPP are given in Figure 1.

All polyelectrolytes including polyphosphates give such curves. According to Fuoss,[8] reduced viscosity in salt-free solutions is related to concentration in the following manner

$$\frac{\eta_{sp}}{c} = \frac{A}{1 + Bc^{1/2}} \qquad (2)$$

A plot of c/η_{sp} vs. $c^{1/2}$ gives a straight line with slope $= B/A$ and intercept $= 1/A$ (recipro-
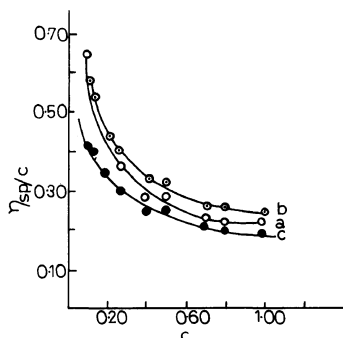
Figure 1. Relations between η_{sp}/c and c for LiKPP samples: $\bigcirc$=(a) Li:K=9:1, sample No. 1; $\odot$=(b) Li:K=8:2, sample No. 7; $\bullet$=(c) Li:K=7:3, sample No. 13.
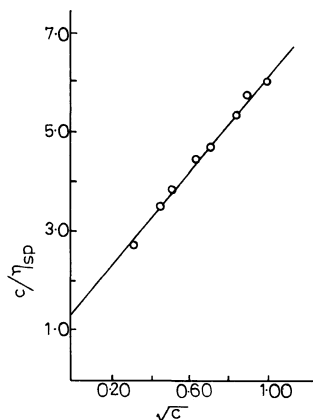
Figure 2. Relation between c/η_{sp} and $\sqrt{c}$ for LiKPP sample (Li:K=9:1); sample No. 1.

cal of intrinsic viscosity in water).

A typical curve of c/η_{sp} against $c^{1/2}$ for one of the samples of LiKPP in salt-free solution is given in Figure 2. The values of c/η_{sp} and $c^{1/2}$ were used to obtain Fuoss equation parameters, A, A/B and B (Table I). Figure 3 shows the dependence of Fuoss equation parameters on molecular weight in the case of LiKPP samples (Li:K=9:1). Similar plots were obtained in other cases also.

On the basis of $\log[\eta]-\log M$ plots it is possible to calculate the values of K and a for the Mark–Houwink relationship

$$[\eta]=KM^a \qquad (3)$$

which can be written as

$$\log[\eta]=\log K+a\log M \qquad (4)$$

Putting $[\eta]=A$ for salt-free solutions

$$\log A = log\,K + a\log M \qquad (5)$$

The best straight line curves consistent with the precision of the experimental points give values of a ranging from 1.84 to 2.02 (Table II). These values are close to the theoretical slope expected for stiff rod-like molecules.[9] The polyphosphate chains become highly extended as the ionic strength of the added salt approaches zero. Van Wazer *et al.*[10] reached similar conclusions on the basis of flow bire-
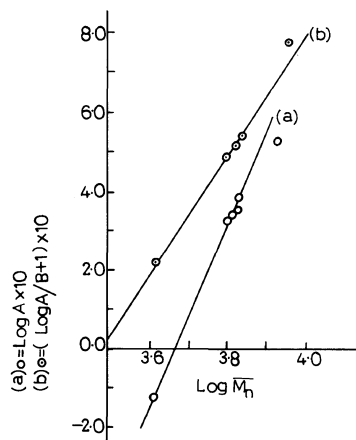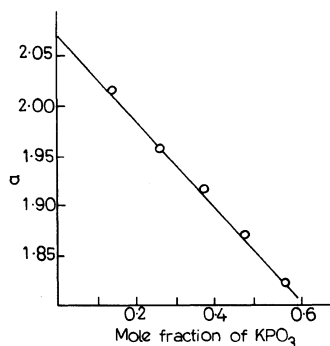

Figure 3. Dependence of Fuoss equation parameters on molecular weights in the case of LiKPP samples (Li:K=9:1); Table I.

fringence measurements.

The parameter B in eq 2 depends on the dielectric constant of the medium.[8] It also determines the degree to which the reduced viscosity is affected by concentration changes. While some authors report that this parameter is independent of molecular weight,[11, 12] this is not true in most cases. The values of B reported in Table I are somewhat scattered. But they show an upward trend with increasing molecular weight. This scattering may be due to a fairly large experimental indeterminacy of parameter A which actually is used in calculat-

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Table II. Dependence of Fuoss equation parameters on molecular weights in the case of LiKPP samples

Ratio	Relationships between A and $\bar{M}_n$	Relationships between A/B and $\bar{M}_n$	Relationships between B and $\bar{M}_n$
9:1	$A=0.40\times10^{-7}\bar{M}_n^{2.02}$	$A/B=1.380\times10^{-7}\bar{M}_n^{1.68}$	$B=0.293\bar{M}_n^{0.19}$
8:2	$A=1.28\times10^{-7}\bar{M}_n^{1.95}$	$A/B=1.703\times10^{-6}\bar{M}_n^{1.40}$	$B=0.075\bar{M}_n^{0.56}$
7:3	$A=1.17\times10^{-7}\bar{M}_n^{1.92}$	$A/B=1.975\times10^{-6}\bar{M}_n^{1.38}$	$B=0.092\bar{M}_n^{0.54}$
6:4	$A=2.25\times10^{-7}\bar{M}_n^{1.87}$	$A/B=2.378\times10^{-6}\bar{M}_n^{1.34}$	$B=0.099\bar{M}_n^{0.52}$
5:5	$A=2.45\times10^{-7}\bar{M}_n^{1.84}$	$A/B=2.577\times10^{-6}\bar{M}_n^{1.34}$	$B=0.096\bar{M}_n^{0.50}$

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

ing B. A typical plot showing dependence of parameters of Fuoss equation on molecular weight is given in Figure 3 for LiKPP samples with Li:K ratio 9:1. Similar plots were obtained with other samples with different Li:K ratios. All of them provided still stronger evidence for the molecular weight dependence of B. If B were independent of the degree of polymerization, the two curves shown in Figure 3 whose ordinates represent $\log A$ and $\log(A/B)+1$, respectively, would be parallel, which they clearly are not. The equations obtained from such sets of curves are given in Table II.

The increase of B with molecular weight is quite in line with our understanding of polyelectrolyte behaviour. While polyions are highly extended at infinite dilution, they tend to coil up more and more as the concentration, and with it the ionic strength, increase. As a consequence, the power of M on which the

reduced viscosity depends should decrease from about 2 at infinite dilution to about 1 when the concentration becomes very large.
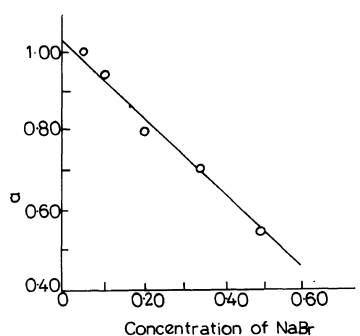
A very interesting relationship is also observed when the values of a are plotted against the mole fraction of KPO_3 (Figure 4). A decrease in its value with increase in the mole fraction of KPO_3 could mean that a is also related to the degree of solvation of the polymer. A decrease in the value of a indicates coiling up of the polymer chain due to decrease in solubility.

(b) Unperturbed Dimensions

The $\log[\eta]-\log\bar{M}_n$ plots in θ solvents were drawn and by the slopes of these plots the values of a could be calculated as given in Table III. The theta solvent is the solution of NaBr at a concentration for which $a=0.5$. For its evaluation in every case, the values of a were plotted against concentration of NaBr. A typical plot is given in Figure 5. The values of θ solvent calculated from these plots are given in Table IV. The concentration of NaBr at which it acts as a θ solvent decreases from $0.58\,N$ to $0.47\,N$ as the mole fraction of KPO_3 increases. Once again, this indicates that solubility decreases with increase in KPO_3 units, and this is quite consistent with our expectations. The decrease in the value of a, the exponent of the Mark-Houwink relation with $0.035\,N$ NaBr as solvent, reported by Bhargava et al.[2] may now be seen in this light. Since a is known to decrease with decrease in solubility[13,14] the results obtained by

Table III. Relevant data for determination of the θ solvent of lithium–potassium copolyphosphate

Ratio Li : K	Concentration of NaBr	a
9 : 1	0.05	0.78
9 : 1	0.10	0.76
9 : 1	0.20	0.70
9 : 1	0.35	0.59
9 : 1	0.50	0.57
8 : 2	0.05	1.01
8 : 2	0.10	0.95
8 : 2	0.20	0.80
8 : 2	0.35	0.71
8 : 2	0.50	0.56
7 : 3	0.05	0.94
7 : 3	0.10	0.84
7 : 3	0.20	0.74
7 : 3	0.35	0.64
7 : 3	0.50	0.54
6 : 4	0.05	0.90
6 : 4	0.10	0.85
6 : 4	0.20	0.74
6 : 4	0.35	0.60
6 : 4	0.50	0.52
5 : 5	0.05	1.16
5 : 5	0.10	1.12
5 : 5	0.20	0.85
5 : 5	0.35	0.65
5 : 5	0.50	0.51

Table IV. Theta solvent data for samples of LiKPP

Serial No.	Ratio Li : K	Mole fraction of KPO_3	θ-Solvent NaBr N
1	9 : 1	0.1325	0.58
2	8 : 2	0.2557	0.56
3	7 : 3	0.3707	0.54
4	6 : 4	0.4731	0.50
5	5 : 5	0.5823	0.47

Figure 6. Plot of normality of NaBr as θ-solvent at 35°C *vs.* mole fraction of KPO_3 for LiKPP samples; Table IV.
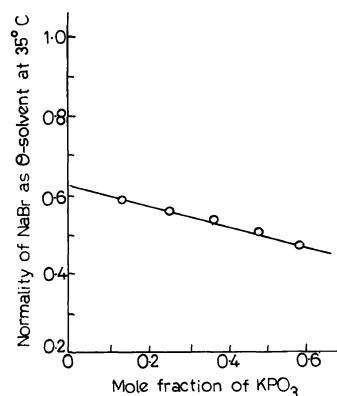

Figure 5. Plots of a *vs.* concentration of NaBr for LiKPP samples (Li : K = 8 : 2); Table III.

Bhargava et al.[2] are in order.

The dependence of a θ solvent on the degree of solvation is illustrated by a plot of the concentration of NaBr (as θ solvent) *vs.* mole fraction of KPO_3 in the copolyphosphate (Figure 6). A progressive decrease in the concentration of NaBr (θ-solvent) with increase in KPO_3 units is clearly observed. It is quite well known that potassium Kurrol salt is insoluble in water and dissolves only in presence of a salt.[6,15]

To calculate the unperturbed dimensions (r_0), the following well known equation[16] was used:

$$[\eta]_\theta = \phi \left(\frac{r_0^2}{M} \right)^{3/2} M^{1/2} = K M^{1/2} \qquad (6)$$

where $[\eta]_\theta$ is the intrinsic viscosity under theta conditions, ϕ is a "universal constant" often referred to as a Flory constant. According to Flory, its value should be close to 2×10^{21}, but workers in the polymer field have found it to

Table V. Unperturbed dimension data for lithium–potassium copolyphosphates

Sample No.	Theta solvent NaBr / N	$[\eta]_\theta$	$r_0 \times 10^{-7}$
1	0.58	0.0688	5.1546
2	0.58	0.0741	6.0673
3	0.58	0.0804	6.3314
4	0.58	0.0847	6.4684
5	0.58	0.0900	6.6267
6	0.58	0.0952	7.4165
7	0.56	0.0635	5.1246
8	0.56	0.0646	5.2856
9	0.56	0.0656	5.8103
10	0.56	0.0741	6.0771
11	0.56	0.0836	6.3988
12	0.56	0.0847	6.9630
13	0.54	0.0519	4.8618
14	0.54	0.0637	5.4275
15	0.54	0.0646	5.7623
16	0.54	0.0738	6.8517
17	0.54	0.0772	6.9566
18	0.54	0.0882	7.3824
19	0.50	0.0479	4.7336
20	0.50	0.0507	4.9056
21	0.50	0.0535	5.0176
22	0.50	0.0699	6.4387
23	0.50	0.0744	6.7375
24	0.47	0.0423	4.7108
25	0.47	0.0439	4.8674
26	0.47	0.0507	5.3518
27	0.47	0.0659	6.1987
28	0.47	0.0704	6.3914
29	0.47	0.0732	6.9319

lie in the range of 2×10^{21} to 3×10^{21}. For some polyelectrolytes, a value close to 2.87×10^{21} has been obtained [17,18]. Eisenberg and King[1] report a value of 2.6×10^{21}. Bhargava and Varma,[19] on the basis of light-scattering experiments, have observed a value close to 2×10^{21} for potassium polyphosphates. We have used a value of 2.1×10^{21} predicted by Flory[16] for all kinds of high polymers.

The values of unperturbed dimensions ob-tained by eq 6 are given in Table V. It is interesting to note that the average unperturbed dimensions of these polyelectrolytes are quite close to those of non-ionic polymers of similar chain architecture,[3] a fact borne out by modern theoretical approaches.

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