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A Contribution to the Physical Chemistry of Colloidal Metaphosphates *

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In a previous paper[1] the results of dispersity measurements on high molecular potassium metaphosphates have been reported. This work is in some points a completion of that mentioned above and the investigations have also been extended to new fields. However, a brief summary of the older investigations will first be given.

I. These colloidal potassium metaphosphates are the salts of Kurol[2], insoluble in water but soluble in solutions of sodium- and ammonium salts. They are prepared by heating primary potassium phosphate:

$$n\ KH_2PO_4 \rightarrow (KPO_3)_n + n\ H_2O$$

If the heating is performed at constant temperature for a long time (150—250 hours) metaphosphates are obtained, the viscosity of which at a given concentration in a defined medium seems to approach a limiting value, corresponding to the temperature in question. $M/50$ basemolar solution in $M/10$ basemolar $Na_3(PO_3)_3$ were used to characterize these substances regarding viscosity.

II. These solutions are too viscous to be used for dispersity measurements. Sedimentation and diffusion were studied in 0.4 M NaCNS where the conditions are more normal.

The sedimentation in the ultracentrifuge[3] proved to be very dependent on concentration; the sedimentation velocity generally increases very much on dilution. The sedimentation constant used in calculations is generally the value at infinite dilution; it is given in Svedberg units, S.

The free diffusion measured by the scale method of Lamm[4] gave a normal picture within the concentration interval 0.1—0.5 %.

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* Part of this investigation was presented at *Sjätte Nordiska Kemistmötet*, Lund, Aug. 1947.

III. If $(KPO_3)_n$ is dissolved in a solution containing an excess of Na^+-ions all the potassium goes into solution, and one can regard a polyanion surrounded by Na^+ ions as the sedimenting and diffusing substance. The partial spec. volume, V, calculated for $(NaPO_3)_n$, was found to be 0.39.

IV. A summary of the temperatures of preparation, viscosity, sedimentas tion and diffusion constants and molecular weights according to Svedberg'-wellknown formula has been drawn up in Table 1. In the table are also given these data for two later syntheses, namely K13 and K14. The molecular weights refer to the original $(KPO_3)_n$.

Table 1. Some molecular constants of the preparations.

Preparation	Temperature of synthesis	Viscosity 10^4 c. g. s.	s_0	D 10^7 c. g. s.	Molecular weight
K12	260°	153	10*	1.7	280,000
K10	290	193	14*	1.4	460,000
K13	305	170	26	1.5	790,000
K 9	382	347	27	1.0	1,100,000
K11	445	460	25	0.6	2,000,000
K14	495	260	34	1.2	1,300,000
K 8	665	422	30	0.6	2,300,000

In the temperature interval investigated the molecular weights seem to increase continuously with the temperature (exceptions, K11 and K14). The molecular weights have also been determined by means of the sedimentation equilibrium method; the results agree rather well with the values of Table 1.

V. In solutions these polymers are highly solvated particles, the shapes of which are probably not spherical.

As these polymetaphosphates are colloidal electrolytes, it is of course interesting to know how the viscosity, for instance, and the sedimentation are affected by electrolytes of different types, and how the charge of the colloidal ion varies in different media. Therefore the viscosity, sedimentation, diffusion and electrophoretic mobility have been studied under various conditions. Attention has also been paid to the question of the stability of the solutions, and the diffusion and sedimentation measurements have been calculated with regard to polydispersity. The problem of molecular shape and structure has been treated with the aid of the electron microscope and X-ray analysis.

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* The preparations K10 and K12 seem to dissociate on dilution as shown by the fact that the sedimentation constant at first increases on dilution, but diminishes when the concentration is less than 0.5 %. The values of the table correspond to the maximal ones. An analogous phenomenon has not been observed with diffusion.

Viscosity

Pascal [2] tried to classify these high polymers by the viscosity of their $M/50$ basemolar solutions in $M/10$ basemolar sodium hexametaphosphate. For this purpose one could of course choose any salt solution in which the polymetaphosphate is soluble, however the result is very dependent on the medium chosen. Independently of the character of the electrolyte the viscosity decreases with increasing electrolyte concentration until salting out of the polymetaphosphate occurs. The effect of the salt may be due to a diminution of the charge of the colloidal anion and a decrease in the solvation.

When investigating the dependence of the viscosity on the ions present in solution one must not forget that the dissolved metaphosphate to some extend contributes to the ionic strength — especially at small concentrations of the low molecular electrolyte. Whence it is suitable to correlate the limiting value $(\eta_{sp}/c)_{c\rightarrow 0}$ against for example the normality of the electrolyte or ionic strength. As is known the specific viscocity η_{sp} is defined by: $\eta_{sp} = \eta_r - 1$; η_r = the relative viscosity. A KPO_3-polymer, preparation K14, has been investigated regarding its viscosity in NaCNS, Na_2SO_4, $Na_3(PO_3)_3$ and $Na_4P_2O_7$, *i. e.* an uni-univalent, an uni-bivalent, an uni-trivalent and an uni-tetravalent electrolyte with the same cation. The measurements have been made at 20° C in a capillary viscosimeter according to Ostwald; they are collected in Table 2. The limiting value $(\eta_{sp}/c)_{c\rightarrow 0}$ has been extrapolated from measurements at four or five concentrations; the curve η_{sp}/c falls to $c = 0$ without showing any minimum. c is expressed in no. of grams of substance per gram of solution.

Table 2. Dependence of the viscosity on the medium.

Medium	$(\eta_{sp}/c)_{c\rightarrow 0}$	Medium	$(\eta_{sp}/c)_{c\rightarrow 0}$
0.05 N NaCNS	645	0.30 N NaCNS	140
0.05 N Na_2SO_4	625	0.30 N Na_2SO_4	200
0.05 N $Na_3(PO_3)_3$	550	0.30 N $Na_3(PO_3)_3$	170
0.05 N $Na_4P_2O_7$	710	0.30 N $Na_4P_2O_7$	280
0.10 N NaCNS	350	0.40 N NaCNS	39
0.10 N Na_2SO_4	446	0.40 N Na_2SO_4	162
0.10 N $Na_3(PO_3)_3$	407	0.40 N $Na_3(PO_3)_3$	156
		0.40 N $Na_4P_2O_7$	245
0.20 N NaCNS	220		
0.20 N Na_2SO_4	261	0.70 N $Na_3(PO_3)_3$	115
0.20 N $Na_3(PO_3)_3$	250	0.80 N Na_2SO_4	118
0.20 N $Na_4P_2O_2$	344	0.80 N $Na_4P_2O_7$	126

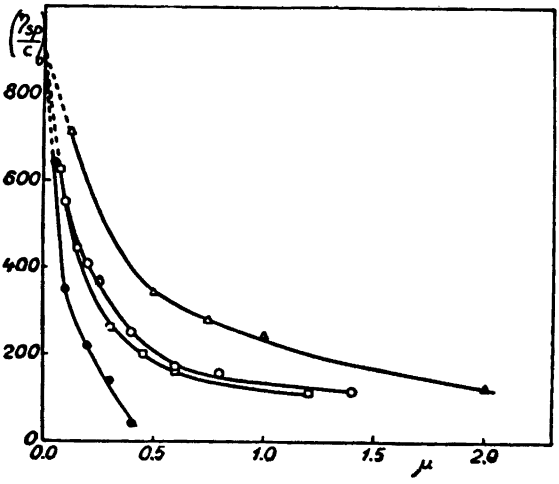

Fig. 1. $(\eta_{sp}/c)_{c\to 0}$ *as a function of the ionic strength.*
● *NaCNS;* □ Na_2SO_4
○ $Na_3(PO_3)_3$; △ $Na_4P_2O_7$

The concentrations at which the polymetaphosphate is salted out by these electrolytes may also be mentioned in this connection. They are: for NaCNS 0.42 *N*, for Na_2SO_4 0.90 *N*, for $Na_3(PO_3)_3$ 0.72 *N*. A saturated solution of $Na_4P_2O_4$ (0.82 *N* at 20° C) does not salt out the metaphosphate.

As is seen from Table 2 the viscosity is not at all the same in, for example, 0.40 *N* NaCNS and 0.40 *N* $Na_4P_2O_7$. However as the great viscosity must be ascribed to the colloidal anion, the effect of electrolytes on the viscosity ought preferably, to depend on the cations present in the solutions if the viscosity were chiefly of an electro-character. Thus the electroviscous effect is only one of the factors acting on these conditions. Unfortunately it is impossible to perform a series of measurements analogous to that of Table 2 in the presence of 2-, 3- or 4-valent cations, as they precipitate the metaphosphate. A rather interesting result is obtained if the limiting value $(\eta_{sp}/c)_{c\to 0}$ is plotted against the ionic strength as abscissa. See Fig. 1.

The ionic strength μ is defined by the expression:

$$\mu = \frac{1}{2} \sum_i c_i z_i^2 \; ; \; c_i = \text{concentration of the ion of valency } z_i.$$

One might expect that the curves extrapolated to $\mu = 0$, would cross the ordinate at the same point which is approximately the case. As is seen from Fig. 1 an uni-univalent electrolyte has the most decreasing influence on the viscosity, followed by uni-bi-, uni-tri- and uni-tetravalent electrolytes respectively.

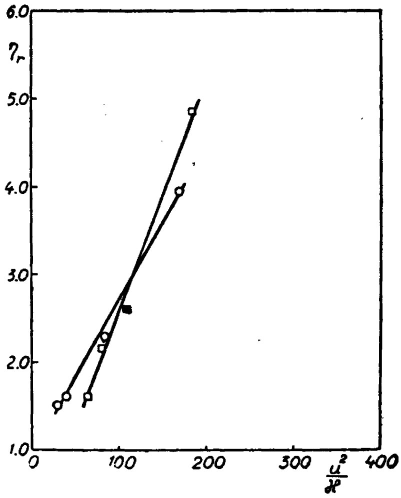

Fig. 2. The relative viscosity as a function of $\frac{\mu^2}{\varkappa}$.
□ *K 14 in* $Na_3\,(PO_3)_3$*-solutions*
○ *K 14 » NaCNS- »*

The addition of an electrolyte causes a denser ionic atmosphere around the particles thus making the approach of the water dipoles to the particles more difficult, which may explain a diminution in the solvation and viscosity. The electroviscous effect has been treated by Smoluchowski[5] and later by Krasny-Ergen[6]. In the formula

$$\eta_r - 1 = 2.5\,\varphi\left[1 + k\,\frac{1}{\varkappa\, a^2\, \eta_0}\left(\frac{\varepsilon\,\xi}{2\,\pi}\right)^2\right] \qquad (1)$$

φ is the volume of the particles relative to the volume of the solution, $\varkappa$ is the specific conductivity of the solution, a the radius of the particles, η_0 the viscosity, ε the dielectric constant of the solvent, ξ the electrokinetic potential of the particles and k a constant; its value being 3/2 according to Krasny-Ergen.

On addition of an electrolyte η_r dereases and this fact is mainly attributed to the increase in conductivity. Eq. (1) has been deduced for a suspended spherical particle and such a picture differs very much from that for a hydrophil colloid such as polymetaphosphate, for which a correcting factor, allowing for the shape, should be introduced in this equation.

If the electrokinetic potential is put proportional to the electrophoretic mobility u (see p. 154) a linear relation is to be expected between η_r and $\frac{u^2}{\varkappa}$, if the other quantities are regarded as constants. In solutions with high electrolyte concentrations such a relation seems to exist, see Fig. 2. Concentration of the polymetaphosphate 0.50 %.

For another colloidal electrolyte, *viz.* polyacrylic acid and its sodium salt Kern[7] has assumed that the viscosity is the product of two factors, the ionic factor, I, and the macromolecular factor, $(\eta_{sp}/c)_m$, allowing for the influence of the charge, and the degree of polymerization respectively.

$$\eta_{sp}/c = I \cdot (\eta_{sp}/c)_m \tag{2}$$

According to Kern an addition of salt only changes the ionic factor, the molecular weight and molecular shape being unchanged. Formally one could apply Eq. (2) to these metaphosphates, but Kern gives no detailed statement of the quantities involved in the ionic factor.

Stability

These polymers are not completely stable in solution[1, 8], as shown by the fact that the viscosity of a solution generally decreases with time. Above all the stability depends on the pH of the solution, but it is also greatly affected by microorganisms[9]; some metaphosphatases degrade the polymetaphosphate. On the assumption that the specific viscosity of the solution can be expressed as

$$\eta_{sp} = \sum_i c_i \eta_i \tag{3}$$

where c_i is the concentration and η_i the viscosity of the i the molecular class, η_{sp} is at least a qualitative measure of the concentration of the high molecular substance, as the contribution of the low molecular components is small. A preparation of $(KPO_3)_n$ K14, has been investigated with regard to the stability at some different pH values. The concentration of the polymetaphosphate was in each case 0.5 %. The ionic strength was 0.3, 0.1 of which was from the buffer substances and 0.2 from NaCl. The results are represented by Fig. 3.

As is easily seen, the metaphosphate solutions are most stable at the neutral point; on the acid side of the pH scale the break-down seems to occur more rapidly than on the alkaline. However as the break-down may occur in many ways, it is of course very difficult to determine a velocity constant of definite meaning, especially as the substance is polydisperse from the beginning. The curves of Fig. 3 can be expressed algebraically in the following manner:

Citrate buffer	pH = 2.0	$\eta_{sp} = 1.366 - 1.34\, t + 0.612\, t^2$
Acetat »	pH = 4.2	$\eta_{sp} = 0.765 - 2.6 \cdot 10^{-3}\, t + 1.3 \cdot 10^{-3}\, t^2$
Phosphate »	pH = 6.9	$\eta_{sp} = 1.191 - 1.7 \cdot 10^{-3}\, t$
Borax-soda »	pH = 9.4	$\eta_{sp} = 1.024 - 1.2 \cdot 10^{-3}\, t$
Borax-NaOH »	pH = 11.5	$\eta_{sp} = 0.958 - 35 \cdot 10^{-3}\, t + 1.4 \cdot 10^{-3}\, t^2$

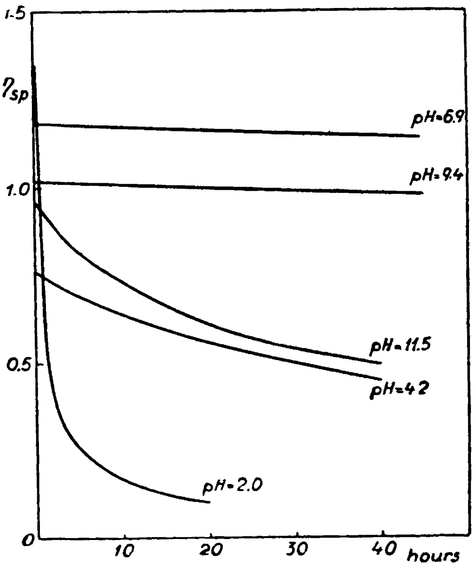

Fig. 3. The change of the specific viscosity with time at different pH-values.

In calculations of the coefficients special consideration has been given to low t-values (t is expressed in hours). The derivatives at $t = 0$, $\left(\frac{d\eta_{sp}}{dt}\right)_{t=0}$ are at these pH-values: -1.34, $-2.3 \cdot 10^{-3}$, $-1.7 \cdot 10^{-3}$, $-1.2 \cdot 10^{-3}$ and $35 \cdot 10^{-3}$ respectively; they may be considered at least as a qualitative measurement of the break-down at these pH values. The breakdown might occur at random. If for instance the PO_3-links were split off one after another, the amount of orthophosphate from hydrolysis would increase to a considerable concentration. By a method of analysis making possible the separation of meta- and orthophosphate is was proved that the orthophosphate formed by hydrolysis is scarcely present in measurable amounts [9, 10]. The orthophosphate can be determined in the colorimeter with ammonium molybdate and ascorbic acid at pH $\simeq$ 5 (acetate buffer) the presence of metaphosphate having no influence on the result.

ELECTROPHORESIS

As the colloidal properties of the polymetaphosphate are to be ascribed to the anion, it is of interest to know its mobility and charge, because these quantities are required for a theoretical treatment of the sedimentation and the diffusion. The electrophoretic measurements required for the calculation of the mobility, have been performed by observing the moving boundary solution/solvent; the method has been worked out by Tiselius *et al.*[11, 12]. The mobility of the colloidal anion u, is expressed in cm^2/s volt (= the velocity in cm/s at the potentialgradient 1 volt/cm). The values of the descending and rising boundary usually agree. At low ionic strengths where differences may occur, u refers to the descending boundary which gives a more accurate value.

The dependence of the mobility on the electrolyte concentration

The measurements of viscosity have clearly shown hos dependent it is on the electrolyte concentration of the solution, and a quantity such as the electrophoretic mobility might be expected to be influenced in a similiar way which is in fact the case. The values of Table 3 refer to 0.50 % solutions of preparation K13.

Table 3. Dependence of the mobility on the medium.

Concentration of the low molecular electrolyte	$u \cdot 10^5$			
	NaCNS	NaCl	Na_2SO_4	$Na_3(PO_3)_3$
0.025 *N*	43	45		53
0.050 *N*	45	36	36	46
0.075 *N*	40			32
0.10 *N*	32	28	27	31
0.20 *N*	22	23	23	31
0.30 *N*	23	22		31
0.40 *N*	22	22	24	32
0.60 *N*			23	
0.80 *N*			23	
»limiting value»	22	22	23	31

In NaCNS, NaCl and Na_2SO_4 approximatively the same limiting value is obtained while that of $Na_3(PO_3)_3$ is considerably greater, which might be due to another state of solution in this medium for instance some kind of complexformation.

As has been shown before, see *e. g.* Table 2, the viscosity of this polymetaphosphate decreases continuously until the salting-out point is reached, while on the other hand the mobility seems to approach a limiting value at a relatively low electrolyte concentration. A possible interpretation is that the ionic charge depends on the concentration of electrolyte in the solution only to a certain extent, whereas the solvation gradually decreases, until the substance is no longer soluble.

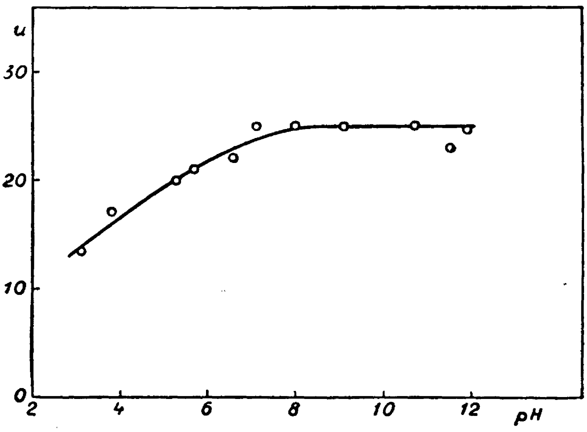

Fig. 4. The electrophoretic mobility as a function of pH.

The dependence of the mobility on the pH value

The dependence of the mobility on the pH of the solution is shown diagrammatically in Fig. 4. The preparation is K14; its concentration in all experiments 0.50 %. The ionic strength was 0.4, of which 0.1 is from the buffer substances and 0.3 from NaCl.

As is seen from Fig. 4 u is constant for basic and neutral reactions whereas the mobility decreases at low pH-values. In solutions more acid than pH $\simeq$ 3 it is difficult to make electrophoretic measurements because the break-down of the polymetaphosphate in acid medium appreciably affects the result. The polyacid, $(HPO_3)_n$ formally corresponding to these metaphosphates is rather strong*. Certainly the pH of a solution in neutral salts is about 6, but

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* The strength of the acid has been estimated in the following manner: Suppose a metaphosphate $(KPO_3)_n$ is dissolved in a solution containing an excess of sodium ions. The process of solution is a permutit reaction resulting in practically all the potassium going into solution if $c_{Na} \gg c_K$. Assume furthermore that there is 1 »effective charge» in m PO_3-links. If we regard these n/m-valent ions as n/m molecules of the uni-univalent electrolyte Na $[Na_{m-1} (PO_3)_m]$ the following expression can be deduced for the dissociation equation of the corresponding acid, for the sake of brevity designed as HA.

$$\frac{C_{A^-}}{\frac{n}{m} C} = \frac{K_s}{C_{H^+} + K_s} \tag{4}$$

K_s = the diss. constant of the acid; c = the conc. of the metaphosphate. Combining the equations at two different pH values (the quantities designed ′ and ″ resp.) yields:

$$\frac{m' c'_{A^-}}{m'' C''_{A^-}} = \frac{C''_{H^+} + K_s}{C'_{H^+} + K_s} \tag{5}$$

this slightly acid reaction is surely due to partial hydrolysis according to the brutto-formula

$$PO_3^- + H_2O \rightarrow H_2PO_4^-$$

Sedimentation

The sedimentation in the ultracentrifuge is also very dependent on the concentration of the low molecular electrolytes. The sedimentation constant s increases on increasing the electrolyte concentration without approaching a limiting value before the metaphopshate is salted out. The variations of the sedimentation constant in different media are shown in Fig. 5. The metaphosphate concentration was 0.50 % in all experiments; preparation K14.

As is seen in Fig. 5 the sedimentation constant at a given concentration of low molecular electrolyte is greatest in NaCl, the s-values diminish when the medium is changed to Na_2SO_4, $Na_3(PO_3)_3$ and $Na_4P_2O_7$ resp. At salt concentrations lower than 0.1 N the sedimentation curves show too great anomalies to be used for accurate calculations. However, it must be emphasized that on dialysing metaphosphate solutions of very low salt concentration against the buffer or water no dialysable metaphosphate has been found. It may therefore be assumed that the state of solution is colloidal even in a medium of low salt concentration.

This difference in the sedimentation constant between various media also remains at infinite dilution, see Fig. 6.

The effect of the low molecular salt on the sedimentation may be twofold. Partly that the presence of an electrolyte diminishes the solvation of the metaphosphate and therefor the frictional resistence on sedimentation, and partly that an excess of electrolyte contributes to decreasing the retarding influence of the charge effect on the sedimentation; the sedimentation constant s_1 of a colloidal ion being lower than would be the case if the particle carried no charge. A theoretical treatment of the subject has been given by Tiselius [13]. For a large excess of low molecular electrolyte the retarding influence of the charge effect is considerably diminished but not completely eliminated. For

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On the assumption that the product $m \cdot c_{A^-}$ is proportional to the charge of the real polyanion and hence its mobility, Eq. (5) can be transformed to

$$\frac{u'}{u''} = \frac{C''_{H^+} + K_s}{C'_{H^+} + K_s} \qquad (6)$$

From Eq. (6) the order of magnitude of K_s can be estimated to be 10^{-3}; the u-values put in Eq. (6) being chosen in the pH-range 3—5.

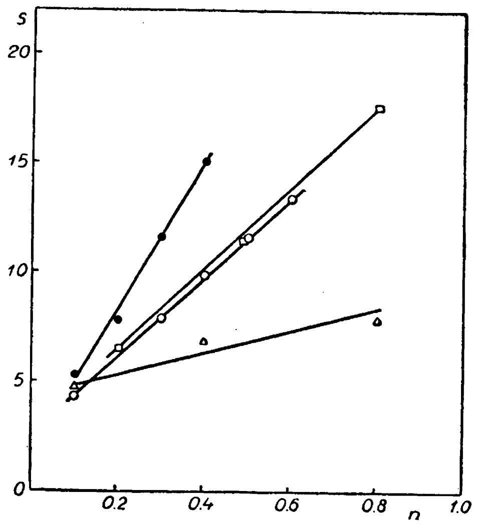

Fig. 5. The variation of s in electrolyte solution of different normalities.

● *NaCl;* □ *Na_2SO_4*
○ *$Na_3(PO_3)_3$;* △ *$Na_4P_2O_7$*

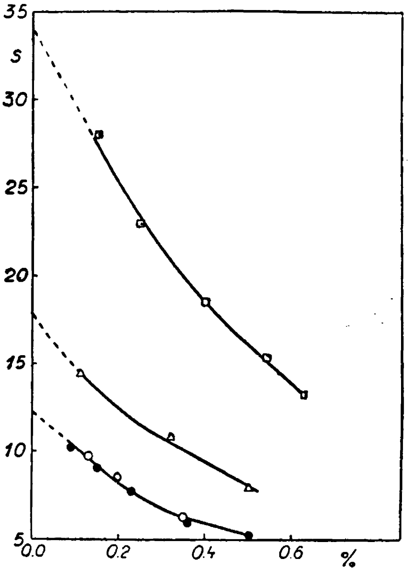

Fig. 6. The dependance of s on the polymetaphosphate concentration in some different electrolytes.

● *0,1-N NaCl;* ○ *0,2 N $Na_4P_2O_7$*
□ *0,4 N NaCl;* △ *0,8 N $Na_4P_2O_7$*

the sedimentation constant of a colloidal electrolyte A_nK in the presence of the salt AB $(C_{AB} \gg C_{A_nK})$ Lamm[14] has deduced the expression:

$$s_1 = \frac{M_1\ (1-V_1\varrho)\left[f_A + (1 + \frac{nc_1}{c}\ f_B\right] - nM\ (1 - V\varrho)\ f_A}{f_K\left[f_A + f_B\ (1 + \frac{nc_1}{c})\right] + \frac{n^2c_1}{c} \cdot f_A \cdot f_B} \tag{7}$$

M_1 and M are the molecular weights of the colloid and the salt resp., V_1 and V the spec. volumes, c_1 and c the molar concentrations, a the density of the solution, f the frictional force on the ion indicated by the subscript and n the charge of the colloidal ion. If the sedimentation constant of the corresponding uncharged particle is s_K, we have:

$s_K = \frac{M_1\ (1 - V_1\varrho)}{f_K}$. Assuming $f_A = f_B$ Eq. (7) can be written

$$\frac{s_1}{s_K} = \frac{1 - \frac{n}{2}\frac{M}{M_1} \cdot \frac{1 - V\varrho}{1 - V_1\varrho}}{1 + \frac{n^2}{2} \cdot \frac{c_1}{c} \cdot f_A/f_K} \tag{8}$$

In 0.4 N NaCl solution, $(1 - V\varrho)$ is calculated to be 0.70; $(1 - V_1\varrho) = 0.61$. $(M = 58.5.)$ Refering to preparation K 14 $c_1/c \simeq 10^{-5}$ in 0.5 % solutions and $M_1 = 1.3 \cdot 10^6$. On the assumption of free ionic mobility $nf_A/f_K = u/u_{\mathrm{Na}}$, a ratio that might be of the order of 1/2. $(u_{\mathrm{Na}}$ is according to Landholt-Börnstein Tabellen $46 \cdot 10^{-5}$ cm^2/s volt.) Putting these values in Eq. (8) we obtain

$$\frac{s_1}{s_k} = \frac{1 - 3n\ 10^{-5}}{1 + 3n\ 10^{-6}} \tag{9}$$

Assuming the molar frictional constant for the colloidal ion to have the same value in sedimentation as in electrophoretic motion the quantity n may be estimated. On this assumption the following expression for the number of effective charges, n_e, is obtained (Tiselius)

$$n_e = \frac{u\ M_1\ (1 - V_1\varrho)}{s_1\ F \cdot 10^7} \tag{10}$$

F = the Faraday const. The n-values calculated from this equation are collected in Table 4. The calculation is based on measurements in 0.4 N NaCl.

Table 4. The effective charge of some preparations in 0.4 N NaCl.

Preparation	Degree of polymerisation	$u \cdot 10^5$	n_e	Number of PO$_3$-groups per unit charge
K12	2400	17	26	90
K10	3900	16	28	140
K13	6600	22	38	175
K14	11000	25	53	210
K11	17000	15	64	260
K 8	19000	18	75	260

The mobility is, if not constant, at least rather independent of the degree of polymerization. This fact might be allowed for by assuming the charge per unit area of the molecules to be the same for all preparations in a given medium.

If the n_e-value of preparation K14 is put into Eq. (9) the charge effect appears to be less than 1 %. The errors of observation are certainly greater, especially as we deal with an unfractionated, polydisperse substance. With regard to the strong dependence of the sedimentation on the electrolyte concentration one might expect a considerably greater correction for the charge effect. Either Eq. (10) is not valid for these metaphosphates, *i. e.* the frictional force on sedimentation and electrophoretic motion is not the same, or it must be assumed that the particle shape and eventually the size also vary with the salt concentration. One might also mention here the fact that s increases from 8 to 15 S (see Fig. 4) when the NaCl concentration increases from 0.2 to 0.4 N, the mobility being constant $\simeq$ 25 within this interval. However, if the charge effects can be omitted in 0.4 N NaCl, n must have very high values in solutions of lower electrolyte concentration. In 0.2 N NaCl n must amount to $\sim$ 15,000 to explain the decrease in the sedimentation constant from 15 to 8 S as a charge effect according to Eq. (9). However, this is impossible since the calculated number of PO_3-groups is less than 15,000.

Diffusion

The free diffusion is, like the sedimentation, very dependent on the electrolyte concentration. At very low salt concentrations the diffusion curves are skew and give a picture which is characteristic of swelling diffusion. At higher salt concentrations these anomalies disappear and the diffusion is more normal. Gralén[15] has worked out a method for the calculation of the diffusion coefficient at infinite dilution D_0, the diffusion being dependent on the concentration. In the formula

$$D_0 = D_m + \frac{A \cdot M_0}{4\ H \cdot t} \tag{11}$$

D_m is the diffusion coefficient calculated by the »moment» method, A the area bounded by the diffusion curve, H the height of the curve and M_0 the distance between the original boundary and the position of the peak after the time t.

However, the D_0-values determined for various media do not differ very much from each other after applying the correction term $\frac{A \cdot M_0}{4\ H \cdot t}$, see Table 5. Preparation K14, metaphosphate concentration 0.50 %. In comparison the diffusion coefficient calculated from the area of the curve D_A is also given; for a polydisperse substance $D_A < D_m$. D is given in 10^{-7} c. g. s.

Table 5. The diffusion coefficient in various media.

Medium	D_m	D_A	Correction	D_0
0.1 N NaCl	1.71	1.48	— 0.84	0.87
0.4 N NaCl	1.34	1.26	— 0.14	1.20
0.2 N $Na_4P_2O_7$	1.50	1.24	— 0.64	0.86
0.8 N $Na_4P_2O_7$	1.21	1.30	— 0.23	0.98

Fig. 7. Electron microscope picture of polymetaphosphate.

As illustrated in Table 5 the correction is considerable especially at low electrolyte concentrations. Of course the charge of the colloidal ion also influences the diffusion. The problem has been theoretically treated by Lamm [14], who for the diffusion coefficient D of the colloidal ion K^{n-} of the compound A_nK in the presence of the low molecular salt AB deduced the expression

$$D = \frac{RT}{f_k} \cdot \frac{1 + \frac{n^2 c_1}{c} \cdot \frac{f_B}{f_A + f_B}}{1 + \frac{n^2 c_1}{c} \cdot \frac{f_B}{f_A + f_B} \cdot \frac{f_A}{\mathrm{f}_K}} \tag{12}$$

where the quantities have the meaning stated before. On the assumption that $f_A = f_B$ and $nf_A/f_K = u/u_{\mathrm{Na}}$ the correction for diffusion in 0.4 N NaCl amounts to 1.5 %, which is much less than the value of Table 5. If the real n-value were greater than the value employed (53) the correction would increase rapidly with increasing n. However, the anomalies appearing on diffusion are probably due not only to charge effects but also to the fact that the substance is largely solvated; the swelling pressure might therefore be of importance.

Molecular weight

In Svedberg's formula for the molecular weight

$$M = \frac{s}{D} \cdot \frac{RT}{1 - V\varrho} \tag{13}$$

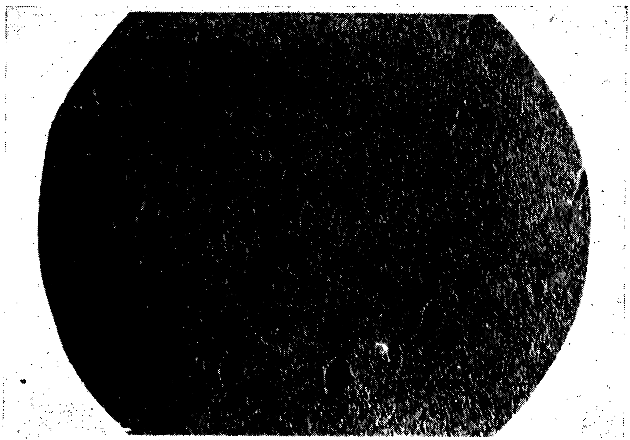

Fig. 8. Electron microscope picture of polymetaphosphate. The preparation is gold-shadowed to obtain a better contrast.

the ratio between the quantities s and D is involved. It appears that this ratio depends on the medium, see Table 6. The values refer to preparation K14, and the molecular weights to the original $(KPO_3)_n$.

Table 6. Dependence of molecular weight on the medium.

Medium	s_0	D_0	s_0/D_0	M
0.1 N NaCl	12	0.87	13.8	640,000
0.4 N NaCl	34	1.20	28.3	1,300,000
0.2 N $Na_4P_2O_7$	12	0.86	14.0	650,000
0.8 N $Na_4P_2O_7$	17	0.98	17.3	800,000

The calculated molecular weight is not constant but varies with the medium. Even if the true correction for the charge effect is considerably higher than the values estimated, this cannot account for the discrepancy between the molecular weights in different media, whence it might be inappropriate to speak of molecular weight in connection with these metaphosphates. Aggregation weight is probably a more correct expression, since all bonds cannot be of head valency character. However, even on this assumption the units held together by head valency bonds must be rather large. In spite of the breakdown of the polymetaphosphate by hydrolysis at weakly acid pH or by enzymes, the solutions still show colloidal properties and only very small amounts of orthophosphate are formed.

Polydispersity

A method of a calculating the polydispersity from the sedimentation curves has been worked out by Gralén[15]. By measuring the width of the curve, B, at successive distance from the centre of rotation, x, the quantity dB/dx is obtained, for which the value at infinite dilution is designated as $\left(\frac{dB}{dx}\right)_0$ By analogy with the assumption of Lansing and Kraemer[16] of a logarithmic distribution of the molecular weights a similar distribution might be assumed for the sedimentation constant

$$\frac{dc}{ds_0} = K_s \cdot e^{-\frac{1}{\gamma_s^2} \ln^2 \frac{s_1}{s_0}} \tag{14}$$

where K_s is the max. height of the distribution curve, γ_s the distribution coefficient of the sedimentation constant and s_1 the sedimentation constant at the max. point. Between $\left(\frac{dB}{dx}\right)_0$ and γ_s we have the relation

$$\left(\frac{dB}{dx}\right)_0 = \gamma_s \cdot \sqrt{\pi} \cdot e^{\gamma_s^2/4} \tag{15}$$

Assuming a logarithmic distribution of the diffusion coefficients

$$\frac{dc}{dD} = K_D \cdot e^{-\frac{1}{\gamma_D^2} \ln^2 \frac{D}{D_1}} \tag{16}$$

where K_D is the maximum height of the distribution curve and D_1 the diffusion coefficient at the maximum point of the curve, we can calculate the distribution coefficient γ_D from Eq. (17)

$$\frac{D_M}{D_A} = e^{3\gamma_D^2/8} \tag{17}$$

These calculations have been applied to part of the material. However, it must be emphasized that the accuracy is very dependent on the possibility of drawing correct base lines to the curves. The values collected in Table 7 are to be considered rather as a measure of the order of magnitude than as absolutely quantitative. The measurements refer to 0.4 N NaCNS as medium.

Table 7. γ_s- *and* γ_D-*values of some preparations.*

Preparation	γ_s	γ_D
K 8	0.12	0.36
K 13	0.10	0.44
K 14	0.17	0.40

The γ_s-values are all higher than the corresponding γ_D-values, probably partly depending on the fact that the diffusion measurements must be extended over several days and that the substance is not stable even at neutral pH. However, these distribution coefficients are still very low compared with those of other polydisperse systems. The following values are reported by Gralén[15]: for cellulose xanthate $\gamma_s = 0.3 — 0.6$ and $\gamma_D = 0.7 — 1.1$; for cellulose nitrate $\gamma_s = 0.1—0.7$ and $\gamma_D = 0.5—1.0$.

In fresh solutions these metaphosphates represent a system of rather low polydispersity in spite of their character of synthetic high polymers.

Molecular shape

Earlier attempts to determine the molecular shape by means of different methods have not given consistent results[2]. It might by expected that a direct measure of the molecular dimensions would be possible by means of the electron microscope. However, a solution of $(KPO_3)_n$ in NaCNS-solution, for instance, placed on to a thin film cannot simply be evaporated for insertion in the focal plane of the electron microscope. The excess of low molecular salt must first be dialyzed away or the metaphosphate would be covered with a salt crust. But when the salt has been dialyzed away the usual state of solution of the metaphosphate is greatly changed and, furthermore, the possibility of agglomeration at evaporation must be allowed for. Thus from the electron microscope pictures it is not possible to draw any valid conclusions concerning the shape and the dispersion of the polymetaphosphates in salt solutions. Fig. 7 shows a rather typical electron microscope picture. The form is irregular, round and rod-like particles are seen together with intermediate forms. Fig. 8 offers a more uncommon picture. Magnification 20,000 times. The pictures cannot represent exactly the molecules or aggregation of molecules as they are to be found in solution. The molecular weight of the preparation investigated is 1,300,000 in 0.4 *N* NaCNS. Thus a single molecule has the weight $1.3 \cdot 10^6 / 6.06 . 10^{23} = 2.1 \cdot 10^{-18}$ g. Supposing the metaphosphate to be flattened on evaporation *in vacuo* the height *h* might be estimated by equating the weight of a particle seen on the plate (area $\sim$ 1—20 mm^2) and particle weight calculated above. (The density of the metaphosphate is 2.5). The *h*-values thus obtained are of the order of magnitude 0.1—1 Å, which values are evidently too low. However, if the electron microscope pictures represent aggregations of 10—100 molecules of the weight mentioned above, *h* might be estimated as several tens of Å's which is more probable. It is obvious, however, that the electron microscope pictures do not represent single molecules such as they are to be found in solution, where they may exist as »geknäuelte Molekeln», which should be treated statistically according to Kuhn.

Solvation

A method given by Sihtola [17] has been applied to the determination of the solvation. After a centrifuge run in a separation cell the buffer remaining in the upper part of the cell is more concentrated than the original buffer, because some water has followed the dissolved metaphosphate to the bottom of the cell. From these concentration differences determined by a refractometric method, the solvation is estimated. The values thus obtained, about 0.6 molecule of water per PO_3-group, are probably too low. (The values refer to 0.4 *N* NaCNS solution.) A co-sedimentation of low molecular electrolyte probably occurs, whence the measured concentration gradient is lower than if there were no co-sedimentation. The question of molecular shape and solvation must be left without a quantitative answer.

X-ray analysis

The synthesis of these polymetaphosphates is in principle the same for all preparations, *viz.* an intermolecular condensation, the degree of polymerisation being dependent on the temperature. Hence it might be assumed that the different preparations are rather alike with regard to structure, which is also confirmed by X-ray powder diagrams obtained by P. H. Lindgren in this institute. The measured spacings are in most cases the same within the errors of measurement although two preparations show interferences which are absent in the others. However, it must be remembered that the powder diagrams are also dependent on the granulation of the preparation, the time of exposure etc. The values of these measurements are collected in Table 8. The wave length of the radiation used, K_α-line of copper, is: $\lambda = 1.539$ A. Even if the preparations are, in the main, very alike these values do not exclude small differences.

Table 8. The spacings of some preparations.

Preparation	Spacing A					
K 12		3.58	3.29	3.00	2.61	2.19
K 9	6.27		3.38	3.07	2.70	2.26
K 14	6.63	4.02		3.14	2.58	2.35
K 8			3.31	3.03	2.63	2.22

SUMMARY

High molecular potassium metaphosphates, the so-called salts of Kurol, have been investigated with regard to their properties in solution.

It has appeared that viscosity, electrophoretic mobility, sedimentation and diffusion velocity are very dependent on the concentration of the low molecular electrolyte in the solutions.

The calculated molecular weights — or perhaps better aggregation weights — differ in various media and seem to increase with the concentration of the low molecular electrolyte in the solution.

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