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A Contribution to the Physical Chemistry of Colloid Metaphosphates II

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In earlier papers[1–3] some problems of the physical chemistry of the colloid metaphosphates have been treated. During the last years, however, the polymetaphosphates have acquired new interest. They have been used as substrates for enzyme studies[4–7], and metaphosphates of high molecular weight have also been isolated from a microorganism, *Aspergillus niger*[8–10]. Accordingly, some further investigations have been carried out in order to get further elucidations of these substances.

The colloid metaphosphates investigated are the salts of Kurol[11], insoluble in water but soluble in solutions of sodium and ammonium salts. They are prepared by heating primary potassium phosphate:

$$n\ \mathrm{KH_2PO_4} \rightarrow (\mathrm{KPO_3})_n + n\ \mathrm{H_2O}$$

If the heating is performed at constant temperature, polymetaphosphates are obtained of which the molecular weight and other related properties correspond to the temperature in question. As shown in a previous paper[3] the molecular weights seem to increase to a limiting value with the temperature of synthesis. A new series of syntheses, the data for which have been drawn up in Table 1, confirms that conclusion. It has not been possible to determine the molecular weights for all preparations but it may be permissable to regard the value of the intrinsic viscosity $(\eta_{sp}/c)_{c \to 0}$ as a qualitative measure of the molecular weight. Van Wazer[12] reports a linear relationship between intrinsic viscosity and degree of polymerisation. His investigation, however, was carried out on preparations of rather low molecular weights, the degree of polymerisation being less than 300. As is well known, $\eta_{sp} = \eta_r - 1$. $\eta_r =$ the relative viscosity, c is expressed in no. of grams of substance per 100 gram of solution.

Table 1. Viscosity and molecular weight of some preparations.

Preparation	Temperature of synthesis	$(\eta_{sp}/c)_{c \to 0}$	Molecular weight
K 17	310°	0.31	
K 18	335	0.33	300 000
K 16	425	0.55	
K 15	500	0.92	1 100 000
K 22	535	1.10	
K 25	585	1.13	
K 24	700	1.18	
K 23	725	1.34	

The measurements have been made in a capillary viscosimeter (Ostwald type) and at 25° C; the medium used is 0.4 *M* NaCl.

The behavior of these polymetaphosphates in solution is determined by two main factors: the charge of the anion and the solvation.

Being colloid electrolytes, the colloid nature of which is due to the anion, these polymetaphosphates are greatly influenced by all factors determining charge and solvation, e.g. the concentration and species of ions present, the presence of dehydrating substances other than salts, as alcohol and glycol.

DISSOCIATION

In a previous paper[3] the net charge for certain preparations has been reported (medium 0.4 *M* NaCl). The calculations were performed according to Tiselius' formula[13], which is derived on the assumption that the frictional force acting upon the molecule during sedimentation equals that during electrophoretic motion. The values thus determined are rather low, corresponding only to about 0.1—1 per cent dissociation. However, it is possible to determine the charge of a colloid ion by means of the Donnan membrane equilibrium. From measurements of the membrane potential at Donnan equilibrium Rinde[14] determined the adsorption of ions on colloidal particles; Adair and Adair[15] calculated the charge of protein molecules. The charge or the degree of dissociation can also be calculated from analytical data. Let us assume the following system: inside the membrane: $(KPO_3)_n$, dissolved in sodium chloride solution; outside: sodium chloride solution. Simplifying the calculations by assuming the same activity coefficients on both sides of the membrane the following equation can be derived for equilibrium conditions:

$$\alpha = 100 \cdot \frac{m}{a} \frac{(c^2 - c_1^2)}{c_1} \tag{1}$$

α = per cent apparent dissociation; m = molecular weight of the base molecule (KPO_3 = 118); a = no. of grams of $(KPO_3)_n$ per liter of solution; c = concentration of chloride ions outside of the membrane and c_1 inside of the membrane.

As c_1 differs from c by not more than a few per cent, eq. (1) can be approximated

$$\alpha = 200 \frac{m}{a} (c - c_1) \tag{2}$$

Certainly it is a very rough approximation to assume the same activity coefficients on both sides of the membrane, but no theory has yet been developed for calculation of activity coefficients of systems involving macro-ions surrounded by clouds of small ions of opposite charge.

A 50 ml sample of polymetaphosphate solution (preparation K 15, dissolved in sodium chloride) was transferred into a cellophane bag and put into a closed cylinder containing about 100 ml of the same sodium chloride solution. The cylinder was then placed in a thermostat. After 3—4 days — the time required for etablishment of equilibrium — the chloride concentrations of the solutions were determined by potentiometric titrations with silver nitrate solution. The results are collected in Table 2.

Table 2. Apparent dissociation under various conditions.

Temperature	Medium	a g/lit.	$(c-c_1)10^4$ mol/lit.	α
5° C	0.10 M NaCl	5.00	26	12
20°	0.40 »	5.00	30	14
	0.20 »	6.00	34	13
	0.10 »	5.97	36	14
	0.05 »	4.77	32	16
25°	0.40 »	8.77	60	16
	0.20 »	6.30	38	14
	0.10 »	5.07	34	16
	0.05 »	4.32	29	16
35°	0.40 »	7.20	83	27

As seen from the table the dissociation calculated according to eq. (2) seems to be rather constant within the NaCl concentration 0.05—0.40 *M*. However, the values of the intrinsic viscosity of preparation K 15 at the same NaCl concentrations, vary over a wide range, see Table 4. This might indicate that the charge effect of the anion on the viscosity is largerly eliminated at 0.05 *M*-concentration and that further addition of salt removes the water of solvation thus decreasing the viscosity. A theory of electroviscous effects in polymer solutions has been given by Hermans and Overbeck [16], but their theory does not take into consideration the solvation, which is possibly the most important property.

The dissociation increases with increasing temperature, but it has not been possible to extend the measurements over a wide range of temperature since the polymetaphosphate is not very stable in solution at high temperature and rather slightly soluble at low temperature.

As has already been discussed in a previous paper [7], the polymetaphosphates form complexes with bivalent metal ions. The equilibrium

$$\text{polymetaphosphate} + \text{bivalent metal ion} \rightleftharpoons \text{complex anion}$$

is displaced to the right. However, the ability of the polymetaphosphate to form complex is limited by the fact that a permanent precipitate is formed if the atomic ratio of bivalent metal to phosphorus (Me/P) exceeds a certain value; for most metals this limiting value is $^1/_3$ *.

Many physico-chemical properties such as viscosity, sedimentation and diffusion constants, specific volume etc. are changed on complex formation. This is probably due to a change of molecular shape, but the apparent dissociation is not influenced.

Measurements of the dissociation of cations from the mangano-polymetaphosphate complex show, within the experimental error, that the dissociation is independent of the presence of Mn^{++} ions. The experimental condition were as follows. Inside the membrane: $(KPO_3)_n$, preparation K 15 dissolved in 0.4 *M* NaCl plus a given amount of $MnCl_2$ solution; outside of the membrane: 0.4 *M* NaCl; temperature 25° C. If c_2 denotes the concentration of free manganous ions inside the membrane, equilibrium conditions give the following expression for the degree of dissociation:

$$\alpha = 200 \cdot \frac{m}{a} (c - c_1) \left(1 + \frac{c_2}{c}\right) \qquad (3)$$

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* A review of the literature dealing with complex-formation between bivalent metals and metaphosphate is given by Karbe and Jander [17]. Investigations on this complex-formation has also been published recently by Van Wazer and Campanella [18].

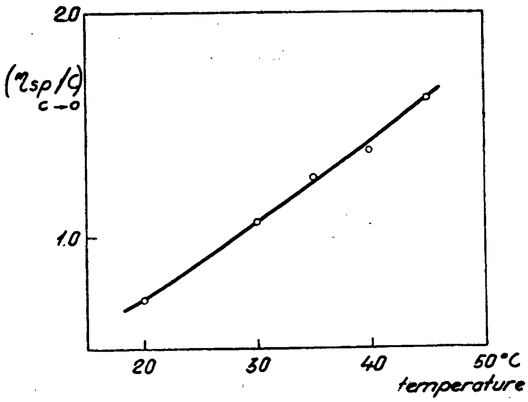

Fig. 1. The intrinsic viscosity as a function of the temperature.

Table 3. Apparent dissociation in the presence of manganese.

a g/lit.	Mn/P	$(c-c_1)\cdot 10^4$ mol/lit.	α
8.33	1 : 64	56	16
8.33	1 : 26	65	18
8.33	1 : 13	47	13
8.33	1 : 7	55	16

where the symbols have the meaning stated before. As c_2 is very small, probably less than 10^{-4}, the correction term is omitted. The results of these measurements, carried out at 25° C, have been collected in Table 3.

VISCOSITY

A condensation product like polymetaphosphate might be expected to be a chain molecule and the work by Van Wazer[19] confirms this assumption. Owing to the fact that these polymetaphosphates show no streaming birefringence in salt solutions of moderate concentration, *i. e.* 0.4 *M* NaCl, (Snellman unpublished) the molecules probably may be assumed to be wrinkled. However, because of the repulsive forces between the negative charges on the big anion it must change shape with increasing or decreasing dissociation. In fact the temperature effect on dissociation and hence on viscosity is very pronounced. For preparation K 15 the intrinsic viscosity has been determined in 0.4 *M* NaCl at different temperatures. The results are shown in Fig. 1 where $(\eta_{sp}/c)_{c\to 0}$ is plotted against temperature. However, as already mentioned, substances other than electrolytes have a great in-

Table 4. Intrinsic viscosity in various media.

Medium	$(\eta_{sp}/c)_{c \to 0}$
0.4 *M* NaCl (water)	0.92
0.3 » »	2.30
0.2 » »	3.40
0.1 » »	5.20
0.1 » (5 % ethanol)	2.95
0.1 » (8 » »)	2.00

fluence on the viscosity of a polymetaphosphate solution. If the salt concentration of such a solution is kept constant but part of the water is substituted with alcohol or ethyleneglycol the viscosity is decreased just as if salts of low molecular weight were added, see Table 4. Preparation used: K 15.

However, it must be remembered that addition of an organic liquid such as alcohol means a change of the dielectric constant of the medium. According to Smoluchowski[20] and Krasny-Ergen[21] the equation for the viscosity of solutions of spherical non solvated particles contains the factor $\frac{\varepsilon^2}{\eta_0}$ in the correction term. η_0 = the viscosity, ε = the dielectric constant of the solvent. The quantity $\frac{\varepsilon^2}{\eta_0}$ is diminished by about 30 per cent when the medium changes from 0.1 *M* NaCl in water to 0.1 *M* NaCl in 10 per cent (by volume) alcohol. This 30 per cent change evidently does not account for the effect of alcohol on the viscosity as shown in Table 3. However, it must be emphasized that the use of Smoluchowski's equation is only an approximation.

ELECTROPHORESIS

The electrophoretic properties of the polymetaphosphates are chiefly determined by the charge of the anion, the solvation being of less importance. At rather low ionic strength ($\mu \sim 0.1$) the mobility has reached a value which does not appreciably change on further addition of salts[3]. However, as might be expected from the dependence of dissociation on temperature, the mobility is subject to a similar dependence. A series of electrophoretic measurements were performed at various temperatures according to the well known technique developed by Tiselius[22] and Svensson[23]. 0.25 per cent solutions of preparation

Table 5. Electrophoretic mobility at various temperatures.

Temperature	$u \cdot 10^5$
5° C	16.4
10	16.9
15	17.9
20	19.2
27	21.3
37	31.7

K 15 in 0.4 *M* NaCl were used for the experiments the results of which have been collected in Table 5. The mobilities, *u*, expressed in cm ^{2}/volt sec., have been calculated by using the conductivity at 20° in order to get comparable values.

The values of the dissociation (*cf.* Table 2) show an analogy to the mobility values. In both cases an increase of the temperature from 5 to 20° C causes only a modest increase of dissociation relative to resp. mobility, whereas another increase to about 35° is accompanished by a more pronounced effect on both dissociation and mobility.

A change of the medium from water to ethanol — water — the concentration of NaCl being the same, 0.1 *M* — decreases the mobility, Table se 6. The variation of the mobility values, however, are of the same order of magnitude as can be expected from the corresponding change of the dielectric constant and viscosity of the medium. If the alcohol is dialyzed off against 0.1 *M* NaCl the mobility is increased almost to its original value. The experiments were performed at + 5° C; concentration of polymetaphosphate 0.30 % (preparation K 15).

Table 6. Electrophoretic mobility in various media.

Medium	$u \cdot 10^5$
0.1 *M* NaCl (water)	17.3
0.1 » (5 % ethanol)	14.4
0.1 » (8 » »)	11.9
0.1 » (8 % ethanol) the ethanol dialyzed off from the polymetaphosphate solution.	15.8

The mobility of the polymetaphosphate anion is but little changed when its constitution is made complex by addition of bivalent metal ions. To 0.30 per cent solutions of preparation K 15 in 0.4 *M* NaCl calcium and mercury were added in the form of 0.15 *M* chloride solutions to the desired quotient, Me/P, and the mixture was dialyzed against 0.4 *M* NaCl before the electrophoresis run. The experiments were carried out at + 5° C. The results have been drawn up in Table 7. The variations of the mobility values are very small, especially when compared with the changes of the intrinsic and specific viscosity values under the same condition (*Cf.* ref. (7)).

Table 7. Electrophoretic mobility of calcium and mercury polymetaphosphate complex.

Metal added	Me/P	$u \cdot 10^5$
Control	—	17.3
Ca	1/9	18.4
Ca	1/4	17.4
Hg	1/9	17.1
Hg	1/6	17.0
Hg	1/3	16.2

SEDIMENTATION

The great dependance of the sedimentation of these polymetaphosphates on the concentration and species of the low molecular weight salts present in the solution has already been discussed in a previous paper[3]. Lamm[24] has theoretically deduced the retarding effect of the charge of a polyvalent ion on the sedimentation. However, the phenomena shown in Fig. 2, where the sedimentation constant S (given in Svedberg units) has been plotted as a function of the salt concentration in various media, cannot be explained by introducing in Lamm's equation the values of the dissociation determined from measurements of the Donnan equilibrium. However, not only low molecular weight electrolytes, but also any substance reducing the solvation is a factor of importance in this case. It must be pointed out that in all experiments the sedimentation curves present only one peak giving an impression of a rather homogenous substance.

The solvation seems to be the dominating factor in this connection. Addition of alcohol or ethyleneglycol to a polymetaphosphate solution has the same

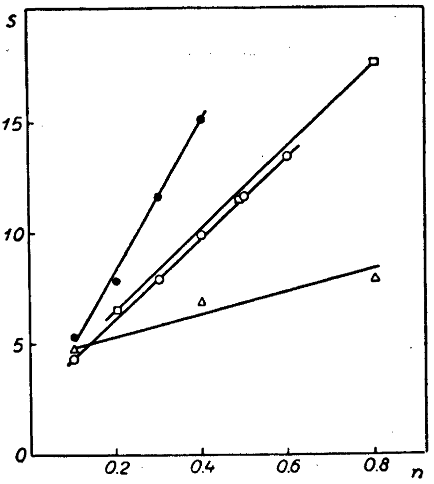

Fig. 2. The variation of s in electrolyte solution of different normalities.

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

effect on the sedimentation constant as an increase of the concentration of low molecular salts to the medium, see Table 8. Solutions of preparation K 15 at a concentration of 0.40 % were used for these experiments; solvent: 0.1 *M* NaCl in different mixtures of alcohol or glycol with water.

The sedimentation constant of the polymetaphosphate anion increases if a bivalent metal ion is bound in the form of a complex. If two alkali metal ions (sodium or potassium) are replaced by a heavy metal ion, *e.g.* mercury, one might assume the increase of the sedimentation velocity to be due to the increased anion weight, but the same phenomenon is observed in the case of a light metal, for instance, magnesium.

Solutions, prepared as follows, were used for the centrifuge runs. To a 0,60 % solution of K 15 in 0.4 *M* NaCl, magnesium and mercury were added in the form of 0.15 *M* chloride solutions to the desired quotient, Me/P. Then the concentration of K 15 was adjusted to 0.40 % by addition of 0.4 *M* NaCl, and

Table 8. Dependance of the sedimentation constant on the medium.

Medium	s
0.1 *M* NaCl (water)	5.9
0.1 » (3 % ethanol)	8.0
0.1 » (5 » »)	9.2
0.1 » (8 » »)	11.5
0.1 » (10 » glycol)	7.1

Table 9. Sedimentation constant of magnesium and mercury polymetaphosphate complex.

Metal added	Me/P	s
Control	—	13.0
Mg	1/6	15.3
Mg	1/3	19.9
Hg	1/6	16.4
Hg	1/3	22.6

the solution was dialyzed against 0.4 *M* NaCl. The results have been drawn up in Table 9.

These results very probably are due to a change of the molecular shape on addition of a bivalent metal. Certainly, it is plausible to assume the bivalent metal acting as a bridge between different molecules or different parts of a single molecule thus causing a change of the molecular size and/or shape. It may perhaps also be possible to regard the surface of the polymetaphosphate molecule as a semipermeable membrane. In that case the concentration of bivalent metal ions on both sides of the surface of a molecule is determined by the Donnan equilibrium.

DIFFUSION

The free diffusion of a polymetaphosphate is, like the viscosity and sedimentation, dependent not only on the concentration of low molecular weight electrolytes; it is also influenced by compounds decreasing the solvation. The dependence on electrolytes and charge effects has been treated in an earlier paper[3]. Here there will be mentioned only some measurements in media containing alcohol and some experiments in which the diffusing anion was a complex with magnesium.

The measurements were made at 20° C by Lamm's[25] scale method, using a steel cell after Claesson:[26] preparation K 15, metaphosphate concentration 0.25 %. The solution of the magnesium-metaphosphate complex was prepared as in the electrophoresis experiments described above (p. 7) and diffused against the outer fluid of dialysis. The results have been collected in Table 10. The diffusion coefficient, D_0, has been calculated according to the moment method; extrapolation to zero concentration after Gralén;[27] D_0 is given in 10^{-7} c.g.s.

As seen in Table 10, the diffusion velocity increases on addition of alcohol and magnesium, probably another indication of changed particle shape or size.

Table 10. Dependance of the diffusion coefficient on the medium.

Medium	D_0
0.1 *M* NaCl (water)	1.05
0.4 » »	1.08
0.1 » (5 % ethanol)	1.25
0.1 » (8 » »)	1.36
0.4 » (water); Mg/P = 1/6	1.20
0.4 » » Mg/P = 1/3	1.39

PARTIAL SPECIFIC VOLUME

In a previous paper[2] the partial specific volume, V, was calculated to be 0.39. This value is not correct but at that time only a small amount of substance was available, thus making accurate determinations rather difficult. In solutions the true value is appreciably smaller. In Table 11 are given some values of V determined in different media. Preparation: K 15. The value 0.39, however, is valid for $(KPO_3)_n$ in the solid state, as determined from measurements on suspensions in organic solvents, e.g. benzene.

A correct value of V is of great importance for calculations of molecular weights. The values tabulated above give molecular weights about 10 per cent lower than those obtained with $V = 0.39$. This means that molecular weights previously published[2, 3] are too low by this amount. However, the order of magnitude of these molecular weights is of primary interest. There is little significance to determinations of molecular weights of polydisperse, unfractionated substances to an accuracy better than 10 per cent.

Table 11. Partial specific volume in various media.

Medium	V
0.1 *M* NaCl (water)	0.311
0.2 » »	0.317
0.4 » »	0.316
0.1 $NaNO_3$ »	0.312
0.1 NaCl (5 % ethanol)	0.315
0.1 » (8 % »)	0.313
0.4 » (water) Mg-complex: Mg/P = 1 : 3	0.370

Fig. 3. Electron microscope picture of polymetaphosphate. Magnification: 30.000.

MOLECULAR SHAPE

Earlier attempts to determine the molecular form have not given consistent results [2, 3]. The data from measurements of viscosity, sedimentation, diffusion *etc.*, are not sufficient for calculation of the molecular dimensions, as the behavior of these polymetaphosphates in solution is probably governed to a high degree by the solvation, which is very difficult to determine quantitatively. However, the absence of streaming birefringence was a reason for assuming that the polymetaphosphates in solution are "wrinkled molecules". (Kuhn: "geknäuelte Molekeln"). Earlier studies with the electron microscope failed to yield further information, because of agglomeration during the preparation.

Usually a diluted solution of the substance to be investigated is evaporated on a thin film of nitrocellulose and inserted in the focal plane of the microscope. (In the case of polymetaphosphates, the low molecular weight salts must, of course, be removed by dialysis to avoid the formation of a salt crust on the film). The nitrocellulose film is negatively charged and the large anions of a polymetaphosphate solution are repelled causing agglomeration, see Fig. 3. This effect can be eliminated or overcome by a technique developed by E. Ribi and Rånby [28]. The nitrocellulose film is first covered with a thin layer of an oxide of a light metal, *e.g.* beryllium, and thus presents a positively charged surface. In this case the metaphosphate anions are attracted to the film, agglomeration is avoided, and the solution can be removed after a very short "wetting" of the film. An electron micrograph thus obtained is shown in Fig. 4.

The diameter of the smallest particles is about one hundred Å units. Assuming spherical form which is a rough approximation, a particle weight of

Fig. 4. Electron microscope picture of polymetaphosphate. The nitrocellulose film is covered with a thin layer of beryllium oxide. Magnification: 30.000.

1×10^{-18} g. is indicated. The molecular weight determined in 0.4 *M* NaCl is 1 100 000, *i.e.* the weight of a single molecule is 1 100 000/6.06 × 10^{23} = 2×10^{-18} g. The two values are of the same order of magnitude. The particles of larger dimensions are formations of irregular shape, such as flattened, wrinkled chain molecules or aggregation of molecules might present.

However, it is very probable that the molecular shape changes with the medium. The values of the molecular symmetry factor, f/f_0, are not consistent in different media (f/f_0 equals 1 for a spherical, non solvated particle: molecular assymetry and/or solvation result in values of f/f_0 greater than unity). A summary of some molecular constants of preparation K 15 is given in Table 12.

Table 12. Some molecular constants determined in various media.

Medium	$(\eta_{sp}/c)_{c \to 0}$	S_0	D_0	M	f/f_0
0.1 *M* NaCl (water)	5.20	14	1.05	480 000	5.2
0.4 » »	0.92	32	1.08	1 100 000	3.8
0.1 » (5 % ethanol)	2.95	20	1.25	570 000	4.1
0.1 » (8 » »)	2.00	25	1.36	650 000	3.6
0.4 » Mg-complex Mg/P = 1/3	0.94	38	1.39	1 000 000	2.8

Assuming spherical molecules the values of f/f_0 can be used for calculation of the solvation. The values thus obtained, 15—40 g of water per gram of polymetaphosphate, are not consistent with the values calculated from the specific hydrodynamic volume, the latter beeing about 5 times higher. As the polymetaphosphate molecules are not perfect spheres but wrinkled chains, both methods of calculation probably give values that are too high but there is no doubt that the molecules are very largely solvated.

SUMMARY

High molecular potassium metaphosphates, the so-called salts of Kurol, have been investigated in solution. The colloid properties are due to the highly charged anion, the influence of which seems to be eliminated at low concentrations of low molecular weight salts ($\mu \sim 0.1$). The solvation has a dominating influence on the physico-chemical properties in media of higher ionic strength.

The molecular constants are dependent on the medium: they are also changed on complex formation between the anion and bivalent metals.

Electron microscope pictures support the view that the colloid polymetaphosphates in solution are wrinkled chain molecules.

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