

STUDIES IN HEXAMETAPHOSPHATES: PART I.

PREPARATION AND PROPERTIES OF SODIUM HEXAMETAPHOSPHATE AND A STUDY OF THE EXTENT OF COMPLEX FORMATION WITH CALCIUM IONS BY CONDUCTIVITY DATA.

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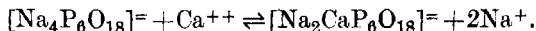
An impure form of sodium hexametaphosphate was prepared by T. Graham (1833) and some of its simple properties were studied by G. von Knorre (1892, 1900), M. Berthelot and G. Andre (1897) and Tantar (1898). G. Tammann (1890, 1892) studied the conductivities of sodium hexametaphosphate solutions in water and concluded that the hexametaphosphate showed conductivity differences characteristic of a dibasic acid.

A detailed study in the preparation and properties of pure forms of sodium metaphosphate was carried out by P. Pascal (1923, 1924, 1932). According to him, sodium hexametaphosphate is best prepared by fusing the trimetaphosphate in small portions at a time in a platinum crucible to about 700°C. and rapidly cooling the fused mass by plunging the bottom of the crucible in cold water. Pascal (1924) also investigated qualitatively the complex forming properties of sodium hexametaphosphate and found that its solutions dissolve calcium oxalate, decolorize ferric thiocyanate and prevent the coloration of uranyl salts by potassium ferrocyanide and concluded that these reactions are possibly due to the formation of the complexes, $\text{Na}_4[\text{Ca}(\text{PO}_3)_6]$, $\text{Na}_3[\text{Fe}(\text{PO}_3)_6]$, and $\text{Na}_4[\text{UO}_2(\text{PO}_3)_6]$.

A renewed and profitable interest in the hexametaphosphates was provided by the discovery of Hall (1934, 1935) that the sodium hexametaphosphate can be used as a very efficient water softener, because it has the power of sequestering calcium and magnesium ions probably due to the formation of the complexes of the type assumed by Pascal. The substance under the trade name of Calgon is now extensively used in water softening and for many other allied purposes (Rosenstein, 1936).

Thomson (1936) showed qualitatively that the complex forming power of the metaphosphate is not limited to alkaline earth ions only.

Ö. Stelling and G. Frang (1941) studied nephelometrically the calcium ion sequestering power of sodium hexametaphosphate and came to the conclusion that an equilibrium of the following type exists:



Campbell and Schenker (1946) carried out a polarographical study of the barium ion removal of the complex metaphosphates and arrived at similar conclusions.

As the above account shows, no systematic attempt has been made to study by quantitative and physicochemical methods the nature and composition of the complexes formed by sodium hexametaphosphate with different ions. In view of the great technical importance of the substance in recent years, it was considered of interest to study the nature of these complexes by different methods. As a result of these investigations extending over a number of years, the nature and composition of these complexes has been elucidated and moreover, many of them have been prepared in the solid state.

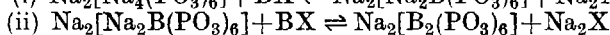
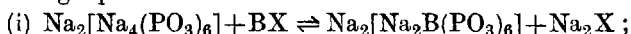
EXPERIMENTAL.

A pure sample of sodium hexametaphosphate was prepared according to the method of Pascal (1923). Microcosmic salt, $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (Merck Extra Pure quality) or mono-sodium di-hydrogen phosphate (Kahlbaum Proanalysis sample) was slowly heated to red heat in a platinum crucible, till the evolution of ammonia and water vapour stopped. The temperature was now gradually raised to about 700° , when the whole mass melted to a clear transparent liquid. The transparent liquid was kept at this red heat temperature from four to six hours and then it was suddenly cooled by dipping the bottom of the crucible in ice cold water, when the liquid solidified to a transparent vitreous mass. Small amounts of the glassy substance thus obtained were again fused as in the above procedure and then suddenly cooled. The small amount of the metaphosphate ensures a rapid cooling of the inner layers of the glass also. The pure hexametaphosphate thus prepared was kept in a desiccator over concentrated sulphuric acid. It has been observed during the course of these studies that the hexametaphosphate thus produced does not show any alteration in its properties over a period as long as ten to twelve months. The substance was powdered finely and dissolved in conductivity water. The substance though quite soluble has a low velocity of solution.

Properties of the sodium hexametaphosphate.—The molecular weight of the sodium hexametaphosphate thus prepared was determined by lowering of the freezing point method and showed a value of the order of 640, after applying the correction due to ionic dissociation in aqueous solution.

A 5% solution of the substance was prepared in water and the reactions with the metallic salt solutions were observed. Solutions of soluble salts of calcium, strontium, barium, magnesium, zinc, manganese, lead, aluminium, beryllium, lanthanum, thorium, zirconium and cerium gave white gelatinous precipitates with the hexametaphosphate solution, but in all the above cases the precipitate thus formed dissolved in excess of sodium hexametaphosphate. The hexametaphosphate solution reacted with ferric and uranyl ions also in such a way as to suppress the tests of these ions altogether so that they gave no coloration with thiocyanate and ferrocyanide respectively.

As demonstrated by the above reactions, the sodium hexametaphosphate has got a sufficiently strong tendency of sequestering calcium, strontium, barium, lead, iron and other ions. This tendency is also exhibited by its property to dissolve insoluble salts—calcium oxalate, strontium carbonate, barium sulphate and lead sulphate. Similar to the reactions postulated by Pascal (1923) and other workers for the dissolution of calcium salts and sequestration of calcium ions, the reactions responsible for the dissolution of the above insoluble salts may be represented by the following equations:



(where BX stands for CaC_2O_4 , CaCO_3 , SrCO_3 , SrSO_4 , BaCO_3 , BaSO_4 , or PbSO_4).

The extent to which the various insoluble salts will go into solution will depend on the 'instability constant' of the complex ion formed and also on the solubility product of the sparingly soluble salt itself. If the above scheme represents the true state of affairs, then on the addition of an insoluble substance like calcium oxalate, the complex sodium calcium hexametaphosphate is formed and the calcium oxalate is replaced by an equivalent amount of soluble sodium oxalate. Therefore, the specific conductivity of the mixture should show an appreciable increase as the reaction proceeds forward and this increment in conductivity will give a measure of the amount of sodium oxalate that has gone into solution and consequently of the calcium oxalate dissolved.

In the following Table I are recorded the conductivities of sodium hexametaphosphate solutions at various dilutions at 30.0°C ., 25.0°C . and 20.0°C . and in the

Tables 2 and 3 are given the conductivities of these solutions when saturated with insoluble salts of calcium :—

TABLE 1.

Concentration of the $\text{Na}_6(\text{PO}_3)_6$ solution.	Conductivities at 30.0° C.		Conductivities at 25.0° C.		Conductivities at 20.0° C.	
	Specific.	Molar.	Specific.	Molar.	Specific.	Molar.
M/8	0.01946	156.2
M/16	0.01116	178.6
M/32	0.00598	191.3	0.004970	159.0
M/64	0.003230	206.7	0.002708	172.8	0.002265	145.0
M/128	0.001749	223.9	0.001451	185.6	0.001284	164.1
M/256	0.000968	247.9	0.000790	202.2	0.000708	181.2
M/512	0.000509	260.8	0.000428	219.1	0.000382	195.8
M/1024	0.0002765	283.1	0.0002375	242.7	0.0002034	208.3
M/2048	0.0001557	318.8	0.0001320	270.0	0.0001117	228.8
M/4096	0.0000890	364.4	0.0000736	301.5	0.0000606	249.0
M/8192	0.0000488	399.7	0.0000409	332.5	0.0000336	275.5

Conductivities of sodium hexametaphosphate solutions when shaken with sparingly soluble salts of calcium.—As stated earlier, the extent of dissolution of the sparingly soluble (or so-called insoluble) calcium salts for example calcium carbonate and oxalate can be found out by the increment in specific conductivity shown by hexametaphosphate solutions when shaken to saturation with these insoluble salts. For this purpose, conductivities of sodium hexametaphosphate solutions were carefully measured and then they were shaken in Jena bottles with pure calcium carbonate and calcium oxalate. The conductivities of these suspensions were measured daily and it was found that the conductivities observed after 3 days differed from those on the next (4th) day by less than 1% in general and hence, this value was taken as the saturation value. During the investigation, blanks were performed by measuring the conductivities of hexametaphosphate solutions after being allowed to stand alone under identical conditions for 4 to 5 days and it was found that these solutions generally did not show a variation in conductivity greater than 1 to 2%. This small difference was ignored and the original conductivities of hexametaphosphate solutions were taken as constant.

TABLE 2.

Specific conductivities at 25.0° C. of sodium hexametaphosphate solutions when alone and when shaken with calcium carbonate and calcium oxalate.

Concentration of $\text{Na}_6(\text{PO}_3)_6$ solution.	Sp. Cond. of the solution alone.	Sp. Cond. of the solution when saturated with calcium carbonate.	Sp. Cond. of the solution when saturated with calcium oxalate.
M/128 ..	0.001454	0.002710	0.002645
M/256 ..	0.000796	0.001498	0.001420
M/512 ..	0.000430	0.000826	0.000820
M/1024 ..	0.000237	0.000537	0.000513
M/2048 ..	0.000132	0.000293	0.000280
Water ..	1.2×10^{-6}	3.21×10^{-5}	1.58×10^{-5}

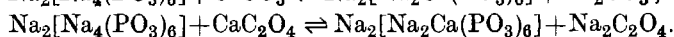
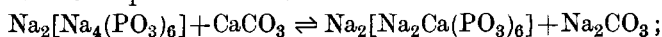
TABLE 3.

Specific conductivities at 30.0° C. of sodium hexametaphosphate solutions when alone and when shaken with calcium carbonate and calcium oxalate.

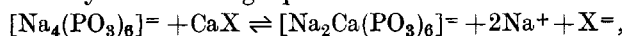
Concentration of Na ₆ (PO ₃) ₆ solution.	Sp. Cond. of the solution alone.	Sp. Cond. of the solution when saturated with calcium carbonate.	Sp. Cond. of the solution when saturated with calcium oxalate.
M/4 ..	0.03340	0.05130	..
M/8 ..	0.01950	0.03350	..
M/16 ..	0.01120	0.01860	..
M/32 ..	0.00592	0.00996	..
M/64 ..	0.003241	0.005563	0.004648
M/128 ..	0.001740	0.003432	0.003243
M/256 ..	0.000961	0.001931	0.001798
M/512 ..	0.000506	0.001098	0.001047
M/1024 ..	0.0002791	0.0006096	0.0006067
M/2048 ..	0.0001562	0.0003393	0.0003346
Water ..	1.4 × 10 ⁻⁶	3.6 × 10 ⁻⁵	1.9 × 10 ⁻⁵

DISCUSSION.

As stated above, the mechanism of the dissolution of calcium carbonate and oxalate has been postulated as:



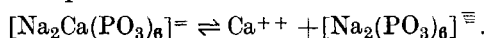
Putting the above equations in the ionic form, the mechanism may be represented by the following equation:



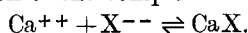
(where X⁻ stands for carbonate or oxalate ion).

The equilibrium of the above reaction, i.e., the extent to which the insoluble salt goes into solution would depend upon the following factors:

(1) *Instability constant or the stability of the complex ion formed.*—The factor would determine the concentration of calcium ions that arises from the secondary dissociation of the complex ions:



(2) *Solubility product of the sparingly soluble salt.*—As shown by the mechanism assumed above, each molecule of the insoluble salt dissolved is replaced by a mole of its anions. These anions will be in equilibrium with the calcium ions, arising from the secondary dissociation of the complex:



So, the dissolution of the sparingly soluble salt will stop at the stage when the ionic product of calcium ions and the anions is equal to the solubility product of the salt dissolved. Thus, in addition to the instability constant of the complex formed, the solubility product of the insoluble salt will also control the extent of its solubility. For example, calcium carbonate has got a greater solubility product than calcium oxalate. So, a greater concentration of carbonate ions will be required than that of oxalate ions, before the solubility product of the corresponding insoluble salt is exceeded. Hence, in the same concentration of sodium hexametaphosphate solution, calcium carbonate will dissolve to a greater extent than calcium oxalate (the solubility being measured in moles of the salt).

(3) *The dilution of the sodium hexametaphosphate solution.*—If the reaction represented by the above equation goes to completion, the molar concentration of the anions of the insoluble salt (appearing in the solution as a result of the dissolution with complex formation) would be equal to the initial concentration of the sodium hexametaphosphate solution. Thus, as the dilution of the hexametaphosphate solution is increased, the concentration of the anions brought into solution as a result of complex formation decreases. Hence, the reaction would have a greater tendency to go to completion in the more dilute solution, as the resulting concentration of the anions being less, there would be a lesser possibility of the solubility product of the insoluble salt being exceeded.

Assuming that the specific conductivity of the complex, $\text{Na}_2[\text{Na}_2\text{Ca}(\text{PO}_3)_6]$, is of the same order as that of the simple sodium salt, $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$, the increase in specific conductivity that occurs when a sodium hexametaphosphate solution is shaken with calcium carbonate or oxalate may be ascribed to the sodium carbonate or sodium oxalate formed plus the specific conductivity of a saturated solution of the sparingly soluble salt. This provides us with a method of finding the concentration of sodium carbonate or oxalate formed in the above cases and thus testing the accuracy of the supposed mechanism and also the correctness of the dependence of the reaction on the various factors enumerated above. To enable us to apply the test at least qualitatively, we have to introduce another approximation, that the solutions are sufficiently dilute so that the conductivity of a mixture might be taken equal to the sum of the conductivities of the constituents. On the basis of these assumptions, the increment in specific conductivity which may be ascribed to the sodium carbonate or oxalate formed, can be calculated easily by deducting the specific conductivity of a saturated solution of the sparingly soluble salt from the actual measured increment in the specific conductivity. In the following Table 4 is given, on the basis of the data recorded in the Table 2, this calculated increment of specific conductivity ascribed to the sodium carbonate alone formed as a result of the dissolution of calcium carbonate in a given solution of the sodium hexametaphosphate. Now, as shown above, if the reaction goes to completion, then the concentration of sodium carbonate formed would be the same as that of the sodium hexametaphosphate itself. Therefore, for comparison is given in the last column of the Table 4, the specific conductivity of a solution of sodium carbonate of the same concentration as that of the hexametaphosphate started with. The close parallelism of the figures in the last two columns of the table indicates the correctness of the assumed mechanism.

The Table 5 records the corresponding data when calcium oxalate is used in place of calcium carbonate.

TABLE 4.

1	2	3	4	5	6
Conc. of hexametaphosphate solution.	Sp. Cond. of the solution.	Sp. Cond. when saturated with CaCO_3 .	Sp. Cond. of a saturated CaCO_3 solution.	Sp. Cond. of Na_2CO_3 formed (3—2—4).	Sp. Cond. of a Na_2CO_3 solution of the same strength as the hexametaphosphate solution.
M/128 ..	0.001454	0.002710	0.000032	0.001224	0.001423
M/256 ..	0.000796	0.001498	0.000032	0.000670	0.000824
M/512 ..	0.000430	0.000826	0.000032	0.000364	0.000436
M/1024 ..	0.000237	0.000537	0.000032	0.000266	0.000227
M/2048 ..	0.000132	0.000293	0.000032	0.000129	0.000117

TABLE 5.

1	2	3	4	5	6
Conc. of hexameta-phosphate solution.	Sp. Cond. of the solution.	Sp. Cond. when saturated with CaC_2O_4 .	Sp. Cond. of a saturated CaC_2O_4 solution.	Sp. Cond. of $\text{Na}_2\text{C}_2\text{O}_4$ formed (3—2—4).	Sp. Cond. of a $\text{Na}_2\text{C}_2\text{O}_4$ solution of the same strength as the hexameta-phosphate solution.
M/128 ..	0.001454	0.002645	0.000016	0.001175	0.001588
M/256 ..	0.000796	0.001420	0.000016	0.000608	0.000841
M/512 ..	0.000430	0.000820	0.000016	0.000374	0.000433
M/1024 ..	0.000237	0.000513	0.000016	0.000260	0.000233
M/2048 ..	0.000132	0.000280	0.000016	0.000132	0.000119

A comparison of the data in the last two columns of the Tables 4 and 5 shows that the concentration of sodium carbonate or the sodium oxalate formed as a result of the dissolution of calcium carbonate or oxalate in sodium hexameta-phosphate solutions is generally of the same order as that of the hexameta-phosphate itself. Thus, the experimental data support the assumed mechanism. The data also show that the difference between the experimental and theoretical values (columns 5 and 6) is, in the more concentrated solutions, much less in the case of calcium carbonate than in the corresponding case of calcium oxalate. A more detailed and quantitative account of these differences will be given in a subsequent communication. Moreover, a perusal of the data in the Tables 4 and 5 clearly shows that both in the case of calcium carbonate as well as oxalate, the reaction does not go to completion in the more concentrated solutions but as the dilution of the hexameta-phosphate solution is increased, the reaction goes to completion or even slightly overshoots the mark. Whether this tendency for the reaction to proceed to the second stage also in the case of calcium salts is real or is only apparent and really due to the approximations made in the present study, would be decided only on more quantitative work. However, at least the correctness of the assumption, that the solubility of the insoluble salt in moles of the salt dissolved per mole of the hexameta-phosphate increases with the dilution of the hexameta-phosphate solution, is established on the above data.

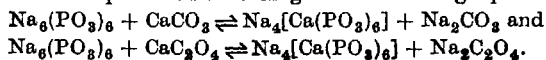
Thus, the increments in specific conductivity which the sodium hexameta-phosphate solutions exhibit when shaken to saturation with calcium carbonate or oxalate are mainly due to the following reaction:



In the following parts of this series will be published more quantitative results obtained by different physico-chemical methods to support and further elucidate the mechanism assumed above.

SUMMARY.

1. The preparation and properties of pure sodium hexameta-phosphate has been described.
2. The conductivities of the sodium hexameta-phosphate solutions have been measured and its power of forming complex ions with Ca^{++} , Sr^{++} , Ba^{++} , Pb^{++} , Mg^{++} , Be^{++} , Zn^{++} , Fe^{+++} , $(\text{UO}_2)^{++}$ and other ions has been demonstrated qualitatively.
3. A study of the mechanism of the dissolution of calcium carbonate and oxalate by the sodium hexameta-phosphate has been made by measuring the increments in specific conductivity which the solutions of sodium hexameta-phosphate exhibit when shaken to saturation with these sparingly soluble salts and from these studies, it has been concluded that the dissolution is due to the formation of complex salts according to the following equations:



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